BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JANUARY, 1941.

I.—ALIPHATIC.

Reaction of hydrogen atoms with butane.—See A., 1941, I, 16.

Manufacture of butadiene.—See B., 1940, 779.

Nitration of aliphatic hydrocarbons. P. G. Stevens and R. W. Schiessler (*J. Amer. Chem. Soc.*, 1940, **62**, 2885—2886). —*l*-CHMeEt·C_5H_{11}-*n*, α_D^{25} −6·5°, and HNO_3 (*d* 1·075) at 130° give *l*-*n*-C_5H_{11}·CMeEt·NO_2, b.p. 106·5—107°, α_D^{25} −0·65° (−0·70°). The mechanism of such nitrations is briefly surveyed. R. S. C.

β-Dioximes and trialkyl*iso*oxazoles from nitroparaffins. S. B. Lippincott (*J. Amer. Chem. Soc.*, 1940, **62**, 2604—2606). —$EtNO_2$ (1), NH_2Pr^a or $NHEt_2$ (1), and H_2O (0·5 mol.) at room temp. give 15% of *ββδ-dioximino-γ-methyl*-n-*pentane*, m.p. 132·2±0·1° (with hot, dil. H_2SO_4 gives 1 mol. of NH_2OH). Pr^aNO_2, NH_2Bu^a or NH_2Pr^a, and H_2O give 57% of *γε-dioximino-δ-ethyl*-n-*heptane*, m.p. 135·4±0·1°, converted by boiling 3N-H_2SO_4 or dil. NaOH into 3 : 4 : 5-*triethylisooxazole*, b.p. 215·3±0·2°/761 mm. Bu^aNO_2, NH_2Bu^a, and H_2O give *δζ-dioximino*-ε-n-*propyl*-n-*nonane* (37%), m.p. 116·6±0·2°, converted by boiling 2N-H_2SO_4 into 3 : 4 : 5-tri-*n*-propyl*iso*oxazole (96%), b.p. 255·2±0·2°. A mechanism for conversion of nitroparaffins into *iso*oxazoles by way of dioximes is proposed. R. S. C.

Manufacture of alcohols from olefines.—See B., 1940, 779.

Catalytic dehydrogenation of alcohols in the liquid phase using ethylene as a hydrogen acceptor. W. Reeve and H. Adkins (*J. Amer. Chem. Soc.*, 1940, **62**, 2874—2876).—Dehydrogenation of liquid aliphatic alcohols (≯C_4) by C_2H_4 in presence of mixed Cu–Zn–Ni–Ba chromite (prep. described) at 280°/70—130 atm. gives 26—77% of the aldehyde or ketone. Examples are Bu^aOH, Bu^βOH, CH_2Bu^γ·OH, *n*-C_6H_{13}·OH, $CHEtBu^a$·CH_2·OH, $C_{12}H_{25}$·OH, heptan-*β*- and -*δ*-ol. Cu chromite is necessary for formation of aldehyde, the other metals (particularly Ba) minimise deactivation of the catalyst, and Zn and Ni minimise condensation of the aldehyde. The reaction is best stopped before all the alcohol is dehydrogenated, as otherwise much aldehyde is lost by condensation. R. S. C.

Rearrangement of unsaturated αδ-glycols. II. *cis*- and *trans*-forms of βε-dimethyl-Δ$^\gamma$-hexene-βε-diol. J. R. Johnson and O. H. Johnson (*J. Amer. Chem. Soc.*, 1940, **62**, 2615—2620; cf. A., 1933, 47).—Me_2 maleate and MgMeBr (6 mols.) in Et_2O, first at −30° to −35° and then at ≯10°, give *cis*-(OH·CMe_2·CH:)$_2$ (**I**) (35%), m.p. 69—70° (configuration confirmed by reactions described below; cf. Bourguel *et al.*, A., 1925, i, 883; 1928, 989, 1353; 1929, 317; 1930, 574), and a mixture (50%), shown to contain *γγ*-dimethylcrotonolactone (**II**) (~15%) and *β*-(? α-)methyl-*γ-iso*hexolactone by hydrogenation (Raney Ni; 25°/6·5 atm.) and conversion into OH·CMe_2·$[CH_2]_2$·CO·NH_2, m.p. 98·5—99·5°, and *γ*-hydroxy-*β*-(? α-)methyl*iso*hexoamide, m.p. 104—106°. Very little (**I**) is obtained at 25°. 30% of (**II**), m.p. 9—9·5°, b.p. 87°/14 mm., 207°/750 mm., is obtained from COMe·$[CH_2]_2$·CO_2Bu^a by MgMeBr–Et_2O at −35°, hydrolysis by boiling 15% KOH–EtOH, and finally acidification. Me_2 fumarate and MgMeBr give only the mixed lactones. *trans*-(OH·CMe_2·CH:)$_2$ (**III**), m.p. 101·5—102·5° (cf. Bourguel *et al.*, *loc. cit.*), is obtained (65%) by condensing $COMe_2$ with (:C·MgBr)$_2$ and reducing the product. As anticipated, the dielectric const. of (**III**) is < that of (**I**). (**I**) is dehydrated by boiling 15% H_2SO_4 or by conc. HCl at −10°, followed by C_5H_5N, to 2 : 2 : 5 : 5-tetramethyl-2 : 5-dihydrofuran, b.p. 100—102°/747 mm. (cf. Zalkind, A., 1923, i, 176), hydrogenated (Raney Ni; 25°/6·5 atm.) to the H_4-derivative (**IV**), b.p. 125—128°, which with HBr in light petroleum gives (CMe_2Br·CH_2)$_2$ (**V**), m.p. 67·5—68·5°). (CH_2·CO_2Et)$_2$ (0·7 mol.) and MgMeBr (2·9 mols.) at −20° give (OH·CMe_2·CH_2)$_2$, dehydrated by 85% H_3PO_4 at 140° to (**IV**), whence (**V**) is obtained. Conc. HCl and (**III**) at −10° give slowly *βε-dichloro-ββε-dimethyl-Δ$^\gamma$*-n-*hexene*, b.p. 175—180°/745 mm., 75—80°/21 mm. Boiling H_2SO_4–AcOH–H_2O (15 : 42·5 : 42·5 parts. by wt.) converts (**III**) into (CH_2:CMe·CH:)$_2$ (**VI**), b.p. 128°/746 mm., 34—35°/18 mm. (maleic anhydride adduct, m.p. 135—136°), and its (?) *dimeride*, b.p. 145—147°/18 mm. (maleic anhydride adduct, sublimes at ~225°), but at room temp. gives (**VI**) and (?) CH_2:CMe·CH:CH·CMe_2·OH, b.p. 145—165°. R. S. C.

Reactions relating to carbohydrates and polysaccharides. LXI. Mechanism of polymerisation of ethylene oxide. S. Perry and H. Hibbert (*J. Amer. Chem. Soc.*, 1940, 62, 2599—2604).—Reactions are described favouring step-wise formation of linear polymerides from $(CH_2)_2O$ (cf. Whitby *et al.*, A., 1928, 627). The degree of polymerisation of the products formed by KOH decreases regularly as the amount of H_2O present is changed from 10 to 0·01 mol. A similar gradual decrease occurs as $(CH_2)_2O$ reacts with increasing amounts of $(CH_2$·$OH)_2$ in presence of a little KOH. Similar results are obtained with H·(O·$[CH_2]_2)_n$·OH (*n* = 2—6 or 18) in presence of NaOH or Na in absence of O_2 and H_2O. The degree of polymerisation increases regularly with time as $(CH_2)_2O$ is polymerised by aq. KOH. The product obtained after completion of the reaction of $(CH_2)_2O$ with H·(O·$[CH_2]_2)_2$·OH reacts further with more $(CH_2)_2O$ to produce products of yet higher mol. wt. and this process may be repeated several times. Polymerides are also formed from $(CH_2)_2O$ with MeOH, EtOH, NH_2Ph, or OH·$[CH_2]_2$·OMe in presence of a little catalyst, but not with $(CH_2$·$OMe)_2$. Dioxan is never formed. R. S. C.

Syntheses of di-β-hydroxyethyl sulphide from ethylene oxide and hydrogen sulphide. H. F. Tseou and T. L. Pan (*J. Chinese Chem. Soc.*, 1939, **7**, 29—32).—$2(CH_2)_2O$ and H_2S with Fe or Al_2S_3 at 340° afford good yields of (OH·CH_2·$CH_2)_2S$ (cf. Tschitschibabin *et al.*, A., 1935, 606). Apparatus is described. A. T. P.

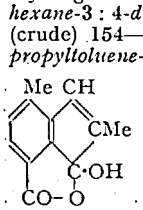
α-Bromo-sulphones. W. M. Ziegler and R. Connor (*J. Amer. Chem. Soc.*, 1940, **62**, 2596—2599).—The SO_2 of α-bromo-sulphones activates the Br for oxidation reactions but deactivates it for metathesis. The increased reactivity of Br in most α-Br-ketones etc. is thus due to preliminary interaction of the CO etc. with the reagent rather than to polar effects. General syntheses of bromo-sulphones are described. *p*-C_6H_4Me·SO_2Me (**I**) with MgEtBr in Et_2O–C_6H_6 gives C_2H_6 and *p*-C_6H_4Me·SO_2·CH_2·MgBr, which with Br in C_6H_6 gives 50% of *p*-C_6H_4Me·SO_2·CH_2Br (**II**), m.p. 89—90°. This method is the most convenient but is not applicable to dialkyl sulphones owing to formation of isomerides. (**II**) is also obtained (33%) from *p*-C_6H_4Me·SO_2Na and CH_2Br_2 in boiling EtOH, but not from (**I**) by Br or NaOBr–$Bu^\gamma OCl$. Bu^aSNa and CH_2Br_2 in boiling, abs. EtOH give (CH_2·$SBu^a)_2$, an oil, oxidised by 30% H_2O_2–AcOH–Ac_2O at 20—40° to (CH_2·$SO_2Bu^a)_2$, m.p. 180—181°, which with boiling KCN–H_2O–EtOH gives 72% of Bu^aSO_2Na. With CH_2Br_2 in boiling EtOH this gives 41% of *CH_2Br Bu^a sulphone* (**III**), m.p. 47—48°. Crude oily Bu^aSO_2·CHEt·CO_2Na, obtained from CHEtBr·CO_2Na and Bu^aSO_2Na in boiling H_2O, with NaOBr at 0° gives 25% of *α-bromo*-n-*propyl Bu^a sulphone*, b.p. 133—136°/5 mm. However, *p*-C_6H_4Me·SO_2·CH_2·CO_2Na and NaOBr at 0° give only (70%) *p*-C_6H_4Me·SO_2·$CHBr_2$ (**IV**), m.p.

116—117°. $Bu^{\alpha}SNa$ and (II) give 76% of (I) and $Bu^{\alpha}{}_2S_2$ (not isolated); p-C_6H_4Me·SNa and (III) give 90% of (p-C_6H_4Mc·S)$_2$ and an oil. MgPhBr and (II) in boiling Et_2O give (I) (59%) and PhBr (77%). C_5H_5N reacts very slowly with (II) or (III) in boiling, abs. EtOH, giving 8% of (p-C_6H_4Me·SO_2·CH_2)$_2$ and 2% of ($Bu^{\alpha}SO_2$·CH_2)$_2$, respectively. NaOEt and (II) in boiling EtOH give 74% of (I) and MeCHO (not identified). (II) and (III) do not react with HI or N_2H_4. (II) does not react with $NHMe_2$ at room temp. or 40—50° or with KCN in boiling 75% EtOH. (III) does not react with boiling NaOAc–EtOH. N_2H_4 and (IV) slowly generate a little N_2. R. S. C.

Syntheses of acetic acid at high pressures.—See B., 1940, 777.

Structure of vinyl polymerides. IX. Catalysts. C. S. Marvel and E. H. Riddle (*J. Amer. Chem. Soc.*, 1940, **62**, 2666—2670; cf. A., 1940, II, 23).—Polymerisation of CH_2:CH·OAc by ultra-violet light gives polymerides, (I) mol. wt. (η) 23,700 and (II) mol. wt. 28,050. KOH–MeOH at room temp. hydrolyses (I) to a glycol, indifferent to HIO_4. Polymerisation by $CdCl_2$ gives a polymeride, mol. wt. 19,400, the glycol from which is also unaffected by HIO_4. These polymerides are both head-to-tail, cross-linked types. BF_3,Et_2O or C_6H_4Me·N_2BF_4 gives black polymerides containing many conjugated ethylenic linkings. CH_2:CHBr·CO_2Me in dioxan in ultra-violet light or with BF_3–Et_2O–PhMe gives polymerides, mol. wt. 11,200 and 6700, respectively, whence Zn removes 85—95% of the Br; they are thus similar. CH_2:CHBr in ultra-violet light or with BF_3,Et_2O gives polymerides, differing physically but both losing Br and HBr to Zn and losing HBr to KI. Polyvinyl chloride loses only 72% of its Cl to Zn and no HCl to KI. R. S. C.

Mechanism of polymerisation. VI. Heat-polymerisation of methyl sorbate, and constitution of the dimeric products. E. H. Farmer and C. R. Morrison-Jones (*J.C.S.*, 1940, 1339—1346; cf. Kuhn *et al.*, A., 1932, 258).—Distillation of the products of heating Me sorbate in CO_2 at 185—235° gives monomeric (6%, chiefly Me sorbate), dimeric (I) (81%), and higher polymeric fractions. Prolonged fractionation and hydrolysis of (I) yields chiefly a semi-resinous acid, with 1-*methyl*-2-*propenyl*-Δ^4-cyclo*hexene*-3 : 4- (II), m.p. 216°, 1-*methyl*-3-*propenyl*-Δ^4-cyclo*hexene*-2 : 4- (III), m.p. 191°, 1-*methyl*-3-*propenyl*-Δ^1-cyclo*hexene*-2 : 4-*dicarboxylic acid* (IV), m.p. 200°, and an (impure ?) acid, m.p. 164—169°. One ester fraction with NH_2·C_6H_4·MgBr gives a *dianilide*, $C_{21}H_{26}O_2N_2$, m.p. 288—290° (decomp.), unaffected by prolonged boiling with MeOH–KOH. AcCl converts (II) into its *anhydride*, m.p. 84°, hydrolysed by boiling H_2O to (II). Hydrogenation (PtO_2) of (II) gives 1-*methyl*-2-n-*propyl*cyclo*hexane*-3 : 4-*dicarboxylic acid*, m.p. 188°, and an acid, m.p. (crude) 154—159°, whilst dehydrogenation (Se) affords 2-n-*propyltoluene*-3 : 4-*dicarboxylic acid*, m.p. 178° (also obtained by Pd–C dehydrogenation), and (V) (?), m.p. (crude) 167—169°, oxidised to 3-oxalylbenzene-1 : 2 : 4-tricarboxylic acid, m.p. 212—216° (decomp.) (*Me*$_3$ ester, m.p. 102°). The ozonide (prepared in EtOAc) of (II) with H_2O, Na_2CO_3, and then $KMnO_4$ at 0° yields AcOH, $H_2C_2O_4$, and CO_2H·CH_2·CMe(CO_2H)·CHMe·CO_2H (VI).



(V.)

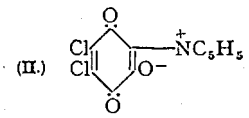
The ozonide prepared in $CHCl_3$ similarly yields AcOH, a trace of $H_2C_2O_4$, and *β-methylbutane-αγδδ-tetracarboxylic acid*, m.p. 169°, which when heated yields (VI). Oxidation ($KMnO_4$) of (II) gives only AcOH and $H_2C_2O_4$. (III) is unaffected by AcCl. Hydrogenation (PtO_2) of (III) yields 4-*methyl*-2-n-*propyl*isophthalic *acid* (VII), m.p. 164°, together with an acid, m.p. (crude) 145—150°, whilst dehydrogenation (Se) gives m-$C_6H_4(CO_2H)_2$. Oxidation ($KMnO_4$ or O_3 in $CHCl_3$) of (III) proceeds as with (II). (IV) is hydrogenated (PtO_2) to (VII), and undergoes no isomerisation with MeOH–KOH or conc. HCl. The mechanism of the formation of the dimerides is discussed, A. Lt.

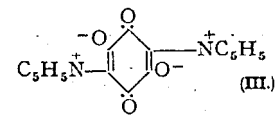
Esters of fatty acids. D. Price and R. Griffith (*J. Amer. Chem. Soc.*, 1940, **62**, 2884).—The following are prepared. Phenacyl nonoate and undecoate, oils, *tridecoate*, m.p. 45—45·5°, *pentadecoate*, m.p. 53·6° (rapid heating), and *heptadecoate*, m.p. 60—60·5°. p-*Phenylphenacyl nonoate*, m.p. 70·8—71·3°, *undecoate*, m.p. 79·5—80°, *tridecoate*, m.p. 86·5—87°, *pentadecoate*, m.p. 91·3—91·8°, and *heptadecoate*, m.p. 95·3—95·8°. *p*-Nitrobenzyl heptoate, nonoate, undecoate, and tridecoate, oils, *pentadecoate*, m.p. 39·5—40°, and *heptadecoate*, m.p. 48·5—49°. R. S. C.

Constitution of arachidonic acid. D. E. Dolby, L. C. A. Nunn, and I. Smedley-Maclean (*Biochem. J.*, 1940, **34**, 1422—1426).—Oxidation of arachidonic acid with alkaline $KMnO_4$ gives $H_2C_2O_4$, AcOH, $BuCO_2H$, and succinic acid, with some HCO_2H, hexoic and glutaric acids. $H_2C_2O_4$ accounts for <50% of the CH_2 groups. Adipic acid is not obtained. The formula
Me·$[CH_2]_4$·$[CH$:$CH·CH_2]_4$·$[CH_2]_2$·CO_2H is suggested.
P. G. M.

Condensations. XIV. Alkylation of ethyl acetoacetate by *iso*propyl acetate in presence of boron trifluoride. D. S. Breslow and C. R. Hauser (*J. Amer. Chem. Soc.*, 1940, **62**, 2611—2612; cf. A., 1940, II, 363).—CH_2Ac·CO_2Et, $Pr^{\beta}OAc$, and BF_3 give 42·1% of $CHPr^{\beta}Ac$·CO_2Et. The mechanism of such reactions of esters is discussed. R. S. C.

Colour reaction of maleic anhydride, *p*-benzoquinone, their partially substituted derivatives, and citric acid. Some zwitterions. A. Schönberg and A. F. A. Ismail (*J.C.S.*, 1940, 1374—1378; cf. A., 1940, II, 35).—Colour reactions with PPh_3 are recorded for 5 maleic anhydride (I) and 12 p-benzoquinone derivatives, some of them requiring heating. Thymoquinone and (I) give colours in absence of solvent. Itaconic anhydride reacts (owing to isomerisation) only in solution. With PPh_3 in C_6H_6, (I) gives a cryst. *betaine*, m.p. ~160°, and an amorphous substance (responsible for the colour) which when heated in CO_2 gives PPh_3. Chloranil with


(II.)


(III.)

C_5H_5N and AcOH or HCO_2H in boiling $CHCl_3$ gives a betaine (II), m.p. >330°. Chlor- or brom-anil or (II) with C_5H_5N in H_2O yields the *dibetaine* (III), m.p. >300°, which with boiling Ac_2O gives a *compound*, $C_{16}H_{10}O_3N_2$, m.p. >300° (*hydrate*). (II) or (III) with boiling aq. Na_2CO_3 or $KMnO_4$ yields C_5H_5N. A. Lt.

***sec.*-Alkyl α-bromo-ketones. I. Reaction with sodium alkoxides. Synthesis of *tert.* acids by rearrangement.** J. G. Aston and R. B. Greenburg (*J. Amer. Chem. Soc.*, 1940, **62**, 2590—2595).—COMe·CMe_2Br (I) and NaOR yield βγ-epoxy-γ-alkoxy-β-methyl-*n*-butane (cf. Ward, A., 1929, 1072), which either rearranges spontaneously to $Bu^{\gamma}CO_2R$ or, if ROH is present, yields OH·CMe_2·CMe(OR)$_2$. NaOMe and (I) in abs. MeOH at room temp. give OH·CMe_2·CMe(OMe)$_2$ (II) (76·5%), b.p. 159—161°/730 mm. (cf. Froning *et al.*, A., 1940, II, 187), hydrolysed by boiling 2% HCl to OH·CMe_2·COMe (III). With 2 : 4 : 1-$(NO_2)_2C_6H_3$·NH·NH_2 in 2N-HCl, (II) gives the 2 : 4-*dinitrophenylhydrazone* (IV), m.p. 139—140°, of (III), but in abs. MeOH gives *γ-methoxy-γ-methyl*-n-*butan-β-one*-2 : 4-*dinitrophenylhydrazone* (V), m.p. 138—139°. NaOEt and (I) in abs. EtOH give 32% of *γγ-diethoxy-β-methyl*-n-*butan-β-ol* (VI), b.p. 110—112°/98 mm., and 17·6% of $Bu^{\gamma}CO_2Et$. (VI) gives, as above, (III), (IV), and *γ-ethoxy-γ-methyl*-n-*butan-β-one*-2 : 4-*dinitrophenylhydrazone*, m.p. 110·5—111°. NaOPr$^{\beta}$–Pr^{β}OH and (I) give 20% of $Bu^{\gamma}CO_2Pr^{\beta}$ and 8% of (?) OH·CMe_2·CMe(OPr^{β})$_2$, b.p. 67—95°/46 mm. Addition of Na (1 atom) and then of (I) (1 mol.) to MeOH (1·5 mol.) in abs. Et_2O gives 39% of $Bu^{\gamma}CO_2Me$ and 12% of (II). NaOEt in Et_2O gives similarly 61·3% of $Bu^{\gamma}CO_2Et$, and NaOPr$^{\beta}$ in Et_2O gives 64% of $Bu^{\gamma}CO_2Pr^{\beta}$. COEt·$CMe_2Br$ (VII) and NaOMe–MeOH give *γγ-dimethoxy-β-methyl*-n-*pentan-β-ol* (65·5%), b.p. 82·5°/100 mm., which yields in 2N-HCl, MeOH, or EtOH the 2 : 4-*dinitrophenylhydrazones*, m.p. 125—126°, 139—139·5°, and 128—129°, of OH·CMe_2·COEt, OMe·CMe_2·COEt, and OEt·CMe_2·COEt, respectively. NaOMe and (VII) in Et_2O give 57% of CMe_2Et·CO_2Me. Boiling aq. KOH and (I) give 76% of (III), which in 2N-aq. HCl gives (IV) and in HCl–MeOH gives (V). *γ-Bromo-γ-methyl*-n-*pentan-β-one*, b.p. 57°/19 mm. (prep. from COMe·CHMeEt), yields similarly *γ-hydroxy-γ-methyl*-n-*pentan-β-one*, b.p. 148—150°/730 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 86—87°). (II) is recovered after treatment with $MgPr^{\beta}Br$–Et_2O, Me_2SO_4–NaOH, or HCl–MeOH, although with the two first-named reagents reaction occurs. R. S. C.

Esters of diacetone alcohol. R. C. Huston and H. E. Ungnade (*J. Amer. Chem. Soc.*, 1940, **62**, 2885).—OH·CMe_2·CH_2·COMe and boiling $(RCO)_2O$ give 70% of CMe_2:CH·COMe and 10—15% of *δ-keto-α-methyl*-n-*amyl*

acetate, b.p. 171—173°/742 mm., 72—73°/10 mm. (*semicarbazone*, m.p. 137·5—138°), *propionate*, b.p. 182—184°/742 mm., 80—81°/8 mm. (*semicarbazone*, m.p. 144·5—145°), and *butyrate*, b.p. 192—193°/742 mm., 97—98°/12 mm. (*semicarbazone*, m.p. 110·4—110·8°). R. S. C.

Synthesis of a new dimethyl-β-methylglucoside. R. E. Reeves, M. H. Adams, and W. F. Goebel (*J. Amer. Chem. Soc.*, 1940, **62**, 2881—2882).—β-Methylglucoside 3-*p*-toluenesulphonate triacetate is converted successively into (by HCl–MeOH at 37°) β-methylglucoside 3-*p*-toluenesulphonate, the CPh_3 ether (*diacetate*, m.p. 145—147°, $[\alpha]_D$ +14·5° in $CHCl_3$) thereof, (Purdie method) 2 : 4-dimethyl-β-methylglucoside 6-CPh_3 ether 3-*p*-toluenesulphonate, and (Na–Hg–EtOH) 2 : 4-*dimethyl-β-methylglucoside*, m.p. 122—123°, $[\alpha]_D^{29}$ −18·6° in $COMe_2$, in 2·5% yield, the intermediates being oils. R. S. C.

Oxidation of aldoses with hypoiodite. VIII. Oxidation of digitoxose with hypoiodite. K. Myrbäck (*Svensk Kem. Tidskr.*, 1940, **52**, 200—203).—Digitoxose is shown to have the glucose-galactose configuration by its rate of oxidation with NaOI. M. H. M. A.

Tetra-acetylaldehydophenylglucosides. R. T. Williams (*J.C.S.*, 1940, 1402—1403).—*p*-OH·C_6H_4·CHO with β-glucose penta-acetate and 10% of anhyd. $ZnCl_2$ or 1% of *p*-$C_6H_4Me·SO_3H$ (Helferich *et al.*, A., 1933, 379) gives poor yields of *p*-aldehydophenyl-β-*d*-glucoside tetra-acetate, $[\alpha]_D^{19}$ −27·9° to −28° in $CHCl_3$ (2 : 4-*dinitrophenylhydrazone*, m.p. 216—218°). *m*-OH·C_6H_4·CHO similarly yields *m-aldehydophenyl-α-d-glucoside tetra-acetate*, m.p. 123—124°, $[\alpha]_D^{22}$ +153·9° in $CHCl_3$ (2 : 4-*dinitrophenylhydrazone*, m.p. 170°), which gives a hard resin when deacetylated (NaOMe in MeOH), whilst *o*-OH·C_6H_4·CHO gives only 3 : 4 : 7 : 8-dibenz-2 : 6 : 9-bis-dioxan. A. Lt.

Cardiac glycoside, m.p. 130°, from *Asclepias curassavica*.—See A., 1940, III, 862.

Nature of the glucosidic linkings in starch. K. Myrbäck (*Svensk Kem. Tidskr.*, 1940, **52**, 126—133).—β-Glucosidic linkings are not present in starch, but vals. of [α] for limit dextrins suggest that a few 1 : 6-α-glucosidic linkings are present. M. H. M. A.

Arylsuphonyl derivatives of ethylenediamine. L. H. Amundsen and R. I. Longley, jun. (*J. Amer. Chem. Soc.*, 1940, **62**, 2811—2812).—$NH_2·[CH_2]_2·NHAc$ and $ArSO_2Cl$ in aq. $NaHCO_3$ at room temp. give *N-benzene-*, m.p. 104·9—105·2°, and *N-p-toluene-sulphonyl-N'-acetylethylenediamide*, m.p. 109·5—109·9°, hydrolysed by boiling aq. HCl to *N-benzene-*, m.p. 172·1—173·6°, and *N-p*-toluene-sulphonylethylenediamine, m.p. 123—124°. Boiling $(CH_2·NH_2)_2$ with $ArSO_2Cl$ in C_6H_6 or by Schneider's method (A., 1896, i, 200) gives *NN'*-di-benzene-, m.p. 168·6—169·3°, and -*p*-toluene-sulphonethylenediamide, m.p. 162·6—163·6°, converted by $ArSO_2Cl$ in $PhNO_2$ at the b.p. (Ar = Ph) or, better for Ar = *p*-C_6H_4Me, 100° into *tetrabenzene-*, m.p. 209—209·7°, and -p-*toluene-sulphonethylenediamide*, m.p. 248·5—249·7°. $N(ArSO_2)_2·[CH_2]_2·NH·SO_2Ar$ could not be obtained. R. S. C.

Action of diazobenzene on alkylacetoacetic ester as method of preparing α-amino-acids and phenylhydrazones of α-keto-acids. I. Synthesis of *iso*leucine and leucine. V. V. Feofilaktov [with L. A. Bogdanova and A. S. Onischtschenko]. **III. Synthesis of alanine.** V. V. Feofilaktov and V. Zajtzeva (*J. Gen. Chem. Russ.*, 1940, **10**, 247—254, 255—259).—An account of work already noted (A., 1940, II, 70).

Action of Grignard reagents on heavy metal salts. V. Formation of olefines in the reaction with silver bromide. J. H. Gardner and C. J. Snyder (*J. Amer. Chem. Soc.*, 1940, **62**, 2879—2880; cf. A., 1939, II, 496; 1940, II, 198).—*n*-C_6H_{13}·MgBr and AgBr in Et_2O at, successively, 0°, room temp., and the b.p. give *n*-$C_{12}H_{26}$ and a little *n*-C_6H_{12} and $CHBu^{\alpha}:CH_2$ (identified as dibromide). R. S. C.

II.—HOMOCYCLIC.

***p*-Bromophenyl*cyclo*pentane.** R. D. Kleene (*J. Amer. Chem. Soc.*, 1940, **62**, 2883).—Addition of Br to phenyl*cyclo*pentane and I gives p-*bromophenylcyclopentane* (55%), b.p. 115—118°/20 mm., oxidised by $Na_2Cr_2O_7$ to *p*-$C_6H_4Br·CO_2H$. R. S. C.

Continuous sulphonation of benzene.—See B., 1940, 777.

Nitration mixtures. I. M. Usanovitsch. **II. Nitration of toluene in presence of acetic acid and nitrobenzene.** M. Usanovitsch and S. Abidov. **III. Nitration of toluene in presence of sulphuric and trichloroacetic acid.** M. Usanovitsch and I. Gluchov. **IV. Nitration of toluene in presence of monochloroacetic acid and ethyl nitrate.** M. Usanovitsch and T. Suschkevitsch (*J. Gen. Chem. Russ.*, 1940, **10**, 219—222, 223—226, 227—229, 230—232).—I. Nitration of aromatic hydrocarbons is effected by $[NO(OH)_2]^{\cdot}$ or $N(OH)_3^{\cdot\cdot}$, but of aliphatic hydrocarbons by NO_3'.

II. In the systems PhMe–HNO_3–AcOH or –$PhNO_2$, the yield of $C_6H_4Me·NO_2$ falls, and of $CH_2Ph·NO_2$ and BzOH rises, with increasing [AcOH] or $[PhNO_2]$. It is concluded that these solvents favour the reactions $N(OH)_3^{\cdot\cdot} + O'' \rightleftharpoons HNO_3 + H_2O \rightleftharpoons [NO(OH)_2]^{\cdot} + OH'$.

III. Max. yields of $C_6H_4Me·NO_2$ are obtained with 1 : 1 HNO_3–H_2SO_4 or 1 : 3 HNO_3–$CCl_3·CO_2H$, and of $C_6H_3Me(NO_2)_2$ with 15 : 85 HNO_3–H_2SO_4. $CH_2Ph·NO_2$ is not formed.

IV. Production of $C_6H_4Me·NO_2$ and $CH_2Ph·NO_2$ falls steadily with rising concn. of the indifferent solvents $CH_2Cl·CO_2H$ or $EtNO_3$. Undissociated HNO_3 is not a nitrating agent. R. T.

Polyalkylbenzenes. XXVII. Preparation of pure ethylbenzenes. XXVIII. Physical properties of tetraethylbenzenes. XXIX. Jacobsen reaction. VII. L. I. Smith and C. O. Guss. **XXXI. Preparation and physical properties of 1 : 2 : 3-trimethylbenzene (hemimellithene).** L. I. Smith and L. J. Spillane (*J. Amer. Chem. Soc.*, 1940, **62**, 2625—2629, 2630—2631, 2631—2635, 2639—2642; cf. A., 1940, II, 301; 1939, II, 306).—XXVII. Controlled passage of EtCl into C_6H_6 (11·27 mols.) and $AlCl_3$ (1·5 mols.) at 70—75° gives readily separable mixtures of 1 : 3 : 5- and less 1 : 2 : 4-$C_6H_3Et_3$, 1 : 2 : 3 : 5- and 1 : 2 : 4 : 5-$C_6H_2Et_4$, C_6HEt_5, or C_6Et_6, the proportions of the products formed being varied at will according to the amount of EtCl used. *vic.* Compounds are not formed. Separation of isomerides depends mainly on smooth sulphonation by $ClSO_3H$ (not H_2SO_4 or SO_3–dioxan) at 0—10° and hydrolysis of the purified Na salts or acids by steam-distillation from 50% H_2SO_4. 1 : 2 : 4 : 5-*Tetraethylbenzene*-3-, $+H_2O$, m.p. 105—107° (amide, new m.p. 123—125°; *anilide*, m.p. 107—108°), and 1 : 2 : 3 : 5-*tetraethylbenzene*-4-*sulphonic acid*, $+H_2O$, m.p. 97—99° (*amide*, m.p. 56—57°; *anilide*, m.p. 78—79°), are described.

XXVIII. The following data, d^{20}, n_D^{20}, and v.p. are recorded. 1 : 2 : 4 : 5-, f.p. 10°, b.p. 246°/734 mm., 1 : 2 : 3 : 5-, f.p. −21°, b.p. 247·4°/734 mm., and 1 : 2 : 3 : 4-$C_6H_2Et_4$, f.p. <−50°, b.p. 251·1°/734 mm.

XXIX. Jacobsen rearrangement of 1 : 2 : 4 : 5- and 1 : 2 : 3 : 5-$C_6H_2Et_4$ or 1 : 2 : 4 : 5 : 3-$C_6HEt_5·SO_3H$ in couc. H_2SO_4 at 100° is very facile. That of C_6HEt_5 is slow and gives poor yields. 1 : 2 : 3 : 4-*Tetraethylbenzene-5-sulphonic acid*, $+H_2O$, m.p. 118—120° (amide, m.p. 103—105°; *anilide*, m.p. 120—121°), is formed in all cases and by distillation in steam from 50% H_2SO_4 at 140° gives ≯90% of 1 : 2 : 3 : 4-$C_6H_2Et_4$. *Pentaethylbenzenesulphonic acid*, $+H_2O$, m.p. 113—115° (*chloride*, m.p. 137—138°; *anilide*, m.p. 140—141°; *Et* ester, m.p. 70—71°), is obtained in 89% yield by $ClSO_3H$ and is readily hydrolysed to C_6HEt_5 by conc. H_2SO_4 at room temp.

XXXI. Prep. of 1 : 2 : 3-$C_6H_3Me_3$, f.p. −25·41±0·05° (corr.), b.p. 176·2±0·1° (*n*, *d*, and v.p. also given), from $CH_2Ph·MgCl$ and paraformaldehyde by way of *o*-$C_6H_4Me·CH_2·OH$ (**I**), *o*-$C_6H_4Me·CH_2Cl$, and 2 : 3 : 1-$C_6H_3Me_2·CH_2·OH$ (**II**) in 26% over-all yield is described. (**I**) is accompanied by large amounts of the formal, and (**II**) by *o*-$C_6H_4Me·[CH_2]_2·OH$. Chlorides are prepared (83—91%) by HCl in light petroleum. Reduction of (**II**) is smoothly (92%) effected by H_2–Cu–Cr_2O_3 at 225°/100—190 atm., but not by other methods. R. S. C.

Polyalkylbenzenes. XXX. Nitration of tetra-, penta-, and hexa-ethylbenzenes. Bromination of the tetraethylbenzenes. L. I. Smith and C. O. Guss (*J. Amer. Chem. Soc.*, 1940, **62**, 2635—2638; cf. A., 1935, 1114).—Addition of HNO_3 (*d* 1·5) to C_6Et_6, C_6HEt_5, or 1 : 2 : 4 : 5-$C_6H_2Et_4$ gives 17%, 69·7%, and 61%, respectively, of 1 : 2 : 4 : 5 : 3 : 6-$C_6Et_4(NO_2)_2$, m.p. 145—147°, converted by $SnCl_2$, followed by $FeCl_3$, into 3 : 1 : 2 : 4 : 5 : 6-O:C_6Et_4:O (73%), m.p. 58—59°. 1 : 2 : 3 : 4- and 1 : 2 : 3 : 5-$C_6H_2Et_4$ give 5 : 6-dinitro-1 : 2 : 3 : 4- (**I**) (68%), new m.p. 117—118°, and 4 : 6-*dinitro*-1 : 2 : 3 : 5-*tetraethylbenzene* (35%), m.p. 93·5—94·5°, respectively. Reduction of (**I**) affords 5 : 6-*diamino*-1 : 2 : 3 : 4-

tetraethylbenzene, m.p. 69—70°, which yields 10 : 11 : 12 : 13-*tetraethylphenanthrophenazine,* m.p. 169—170°, and 2-*methyl*-4 : 5 : 6 : 7-*tetraethylbenziminazole,* m.p. 241—242°. Bromination in $CHCl_3$ or AcOH gives 3-*bromo*-1 : 2 : 4 : 5-, m.p. 9°, b.p. 149°/9 mm., 4-*bromo*-1 : 2 : 3 : 5-, b.p. 150°/9 mm., and 5-bromo-1 : 2 : 3 : 4-tetraethylbenzene, b.p. 152°/9 mm., and in $CHCl_3$ 3 : 6-dibromo-1 : 2 : 4 : 5- (**II**), m.p. 112—113°, 4 : 6-*dibromo*-1 : 2 : 3 : 5-, m.p. 48·5—49·5°, and 5 : 6-dibromo-1 : 2 : 3 : 4-tetraethylbenzene, m.p. 76—77°. Nitration of (**II**) gives a small amount of a (?) dibromotrimethylbenzyl nitrate, m.p. 120—122°. R. S. C.

Reaction of polystyrenes with bromine [and with benzoyl hydrogen peroxide]. L. Marion (*Canad. J. Res.*, 1940, **18, B,** 309—317).—Attempts to detect a double linking in polystyrenes by BzO_2H gave low results. The reaction with Br depends greatly on concn., but in the more dil. solutions some Br is added. F. J. G.

Dehydrogenation. II. Elimination and migration of methyl groups from quaternary carbon atoms during catalytic dehydrogenation. R. P. Linstead, S. L. S. Thomas, and (in part) K. A. O. Michaelis (*J.C.S.*, 1940, 1127—1134).—The dehydrogenation of *cis*-9-methyl-deca- (**I**) or -octa-hydronaphthalene (**II**) vapour at 300—330° (cf. A., 1937, II, 406) is further examined, with that of other hydronaphthalenes. Catalysts of increased activity are obtained when the method of Willstätter *et al.* (A., 1921, ii, 186) is modified by pptg. the metal at a higher dilution, with stirring. Pt and Pd catalysts give similar results, although Pd apparently has a greater tendency to cause side reactions. In activity, metal–C > metal–asbestos > metal as " black." The course of dehydrogenation of substances containing quaternary C varies with the carrier. Catalysts on asbestos produce greatest migration of angular Me, and approx. equal elimination; the latter strongly predominates with catalysts on C. Thus (**I**) and (**II**) give, with Pt–C, $C_{10}H_8$ and CH_4, and, with Pt- or Pd–asbestos, these and 1-$C_{10}H_7Me$ (**III**). Of possible mechanisms of migration of Me from $C_{(9)}$ to $C_{(1)}$, that of ring-opening between $C_{(1)}$ and $C_{(9)}$, with re-formation at $C_{(5)}$, is excluded by dehydrogenating *cis*-4 : 9-dimethyloctahydronaphthalene (**IV**) to 1 : 5-$C_{10}H_6Me_2$ (**V**) (cf. *loc. cit.*). Initial purity of (**IV**) is now established by cyclising 2 : 6-dimethyl-1-Δ$^{\gamma}$-butenyl*cyclo*hexanol by AcOH–Ac_2O–H_2SO_4 to cis-4 : 9-*dimethyldecahydro-α-naphthol,* m.p. 93°, b.p. (crude) 132—142°/13 mm., which with $KHSO_4$ at 194° gives (**IV**), dehydrogenated by Pt–C and Pt–asbestos to (**III**) and to (cryst.) (**V**), as main products respectively. A second possible mechanism, intermediate formation of a C_3-ring involving $C_{(1)}$ or $C_{(8)}$, would with cis-1 : 9-*dimethyloctahydronaphthalene* (VI), b.p. 87°/8—9 mm., imply formation either of a *cyclo*butane ring at $C_{(1)\text{ and }(9)}$ or of a *cyclo*propane ring at $C_{(8)\text{ and }(9)}$, and thus of 1-$C_{10}H_7Et$ or of 1 : 8-$C_{10}H_6Me_2$, respectively. Actually (**VI**), prepared by $H_2C_2O_4$-dehydration of cis-1 : 9-*dimethyldecahydro-α-naphthol* [from *cis*-1-keto-9-methyldecahydronaphthalene (Grignard)], is unaffected by Pt–asbestos at 335°, and with Pt–C gives (**III**), with no higher homologue. A third possible mechanism is migration of a hydrocarbon fragment.

Of *gem*-Me_2 compounds, 1 : 1-dimethyltetrahydronaphthalene (**VII**) over Pt–C at 305° gives (**I**) as main product, but over Pd–C at 315° in a continuous circulation apparatus gives also some 1 : 2-$C_{10}H_6Me_2$. 1 : 1 : 6-Trimethyltetrahydronaphthalene (ionene) over Pt–asbestos or Pd–C at 305—330° gives 1 : 6-$C_{10}H_6Me_2$ (synthesised by Clemmensen reduction of 1-keto-4 : 7-dimethyltetrahydronaphthalene, prepared from γ-*p*-tolylvaleryl chloride and $SnCl_4$), no $C_{10}H_5Me_3$ being detected. There is thus much less tendency for Me to migrate from a *gem* than from an angular group. Resistant hydrocarbons with catalysts on C at ≮325° evolve gas copiously and apparently in part give smaller fragments, the yield of liquid products falling to ~70%. In two experiments, (**VII**) and Pt–C at ~320° gave, during early stages, some $C_{10}H_8$ [due to transitory presence in the catalyst of abnormally active centres (?)], as did (**VI**). E. W. W.

Ozonisation of hydrindene. L. Long, jun. and L. F. Fieser (*J. Amer. Chem. Soc.*, 1940, **62**, 2670—2673).—Ozonisation of hydrindene (**I**) in EtCl at −30° or AcOH at room temp. and subsequent hydrogenation (Pd–$CaCO_3$) gives up to 60% of 1-hydrindone with $(CHO)_2$ (up to 1·4% isolated as *p*-nitrophenylosazone or glyoxime) and $(CH_2{\cdot}CO_2H)_2$ (up to 11·4%). Reaction in other solvents is less satisfactory. 62·5% of $(CH_2{\cdot}CO_2H)_2$ is obtained by ozonisation of *cyclo*pentane-1 : 2-dione (modified prep.), f.p. 0° [dioxime, m.p. ~190° (decomp.)], and probably originates therefrom in the decomp. of (**I**). Thus, the Mills–Nixon orientation of ethylenic linkings (A., 1931, 83) in (**I**) is preferred. R. S. C.

Determination of acenaphthene.—See B., 1940, 778.

Abnormal acetoacetic ester synthesis. II. Reaction of sodium with fluorene and benzyl benzoate. H. F. Tseou and T. S. Chow (*J. Chinese Chem. Soc.*, 1939, **7**, 27—28).—Fluorene, $CH_2Ph{\cdot}OBz$ and Na at 170—190° (13 hr.) afford 9-benzylfluorene, m.p. 131°, and BzOH; no 9-benzoylfluorene is obtained. A. T. P.

Aromatic cyclodehydration. VII. Phenanthrene. C. K. Bradsher and R. W. Wert (*J. Amer. Chem. Soc.*, 1940, **62**, 2806—2807; cf. A., 1940, II, 271).—*o*-$C_6H_4Ph{\cdot}MgI$ and MeCHO in Et_2O give 56% of α-*o-diphenylylethyl alcohol,* m.p. 110·5—111·5°, dehydrated by $KHSO_4$ at 160° to *o*-$C_6H_4Ph{\cdot}CH{:}CH_2$ (24%), b.p. 127—130°/5 mm. *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ in Et_2O then gives an oxide (not isolated), which in boiling HBr–AcOH affords a little phenanthrene (**I**). Crude *o*-$C_6H_4Ph{\cdot}CH(OH){\cdot}CH_2{\cdot}OMe$, obtained from *o*-$C_6H_4Ph{\cdot}CO{\cdot}CH_2{\cdot}OMe$ by $Al(OPr^{\beta})_3$, with boiling HBr–AcOH gives 46% of (**I**). R. S. C.

Determination of phenanthrene.—See B., 1940, 778.

Polycyclic aromatic hydrocarbons. XXVI. C. L. Hewett and R. H. Martin (*J.C.S.*, 1940, 1396—1398).—Paraformaldehyde with HCl in glacial AcOH, followed by 1 : 2 : 3 : 4-$C_6H_2Me_4$, yields 2 : 3 : 4 : 5 : 2′ : 3′ : 4′ : 5′-*octamethyldiphenylmethane,* m.p. 146—147°, and 2 : 3 : 4 : 5 : 1-$C_6HMe_4{\cdot}CH_2Cl$, which is converted via the nitrile and acid into $C_6HMe_4{\cdot}CH_2{\cdot}CO_2Na$. This with *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ and Ac_2O yields o-*nitro*-, m.p. 214—215°, reduced ($FeSO_4$) to o-*amino*-α-2′ : 3′ : 4′ : 5′-*tetramethylphenylcinnamic acid,* m.p. 235—236°, which when diazotised and treated with Cu powder yields *Me o-hydroxy*-α-2′ : 3′ : 4′ : 5′-*tetramethylphenylcinnamate,* m.p. 172—173°, and 1 : 2 : 3 : 4-*tetramethyl*-10-*phenanthroic acid,* m.p. 226—227°, decarboxylated (Cu-bronze in quinoline) to 1 : 2 : 3 : 4-*tetramethylphenanthrene,* m.p. 92—93° [picrate (unstable); *s*-$C_6H_3(NO_2)_3$ *complex,* m.p. 161—162°]. A. Lɪ.

Fluorescence of hydrocarbons and of their mixtures with naphthacene. F. Weigert (*Trans. Faraday Soc.*, 1940, **36**, 1033—1035).—Experiments illustrating the influence of a minute proportion of naphthacene on the fluorescence of 1 : 2 : 5 : 6-dibenzacridine and a no. of condensed hydrocarbons in $COMe_2$ solution and in microcryst. suspensions are described. F. L. U.

Hydrogenation of aniline.—See B., 1940, 842.

Nitro-derivative of 2-bromo-*m*-4-xylidine. W. C. Spitzer (*J. Amer. Chem. Soc.*, 1940, **62**, 2884).—1 : 3 : 2 : 4-$C_6H_2Me_2Br{\cdot}NHAc$ and H_2SO_4–HNO_3 at <15° give the *Ac* derivative, m.p. 171—172° (hydrolysed by boiling 50% H_2SO_4), of 2-*bromo*-6-*nitro*-4-m-*xylidine,* m.p. 129—130° (sublimes), which gives (diazo-reaction) 1 : 3 : 2 : 4-$C_6H_2Me_2Br{\cdot}NO_2$. R. S. C.

Sulphonation of ethylaniline. G. V. Shirolkar, I. S. Uppal, and K. Venkataraman (*J. Indian Chem. Soc.*, 1940 **17**, 443—448; cf. A., 1939, II, 150).—NHPhEt yields with 20% oleum at 185—190°, *p*-, and with 20% oleum at 50—60° followed by more conc. oleum at <40°, a mixture (proportions depending on concn. of oleum) of *p*- and *m*-$NHEt{\cdot}C_6H_4{\cdot}SO_3H$. *N*-Ethylaniline-*o*-, m.p. 212—213° (decomp.) (from *o*-$NH_2{\cdot}C_6H_4{\cdot}SO_3H$, Et_2SO_4, and Na_2CO_3), -*m*-, and -*p*-sulphonic acids with *p*-$C_6H_4Me{\cdot}SO_2Cl$ and C_5H_5N yield the *p*-toluenesulphonyl-*N*-ethylanilinesulphonic acids (*p*-$C_6H_4Cl{\cdot}NH_2$ salts, m.p. 181—183°, 111°, and 217—218°, respectively), also prepared by ethylating (Et_2SO_4) the *p*-$C_6H_4Me{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_3H$. A. Lɪ.

[Sodium *p*-α-sulphoethylaminobenzenesulphonamide] therapeutic product of sulphanilamide class.—See A., 1941, III, 33.

Soluble aromatic sulphonamide compounds.—See B., 1940, 897.

Nitrogenous compounds of mercury as promoters of the chemical activity of selenium, and their rôle in the preparation of azo-compounds, azines, and dyes from arylamines by the action of sulphur or selenium. P. S. Pischtschimuka (*J. Gen.*

Chem. Russ., 1940, **10**, 305—318).—Dehydrogenation of aromatic amines by S or Se, with production of hydrazo- and azo-compounds, azines, thiazines (selenazines), and their coloured derivatives is catalysed by Hg compounds in which Hg is attached directly to N. For NH_2Ph and $Hg(NHAc)_2$ the yield of NPh:NPh rises in the series: no solvent, C_5H_5N, EtOH, PhMe, $C_6H_4Me_2$, CCl_4, ligroin (b.p. 90—110°), light petroleum (b.p. 45—65°), $CHCl_3$, *cyclo*hexane, C_6H_6; in C_6H_6 the yield rises in the order: HgO, $Hg(NHPh)_2$, $HgNH_2Cl$, Hg phthalimide, Hg succinamide, $CO(NH)_2Hg$, $HgCN_2$, Hg succinimide, $Hg(NHAc)_2$, $Hg(NHBz)_2$. With $Hg(NHAc)_2$ in C_6H_6, the yield of azo-compound rises in the order: *o*-$C_6H_4Me{\cdot}NH_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}N{:}NPh$, *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$, *m*-xylidine, *m*-$C_6H_4Me{\cdot}NH_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}OMe$, *m*-$NH_2{\cdot}C_6H_4{\cdot}NO_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}NO_2$, NH_2Ph, *p*-$C_6H_4Me{\cdot}NH_2$, *o*-toluene azotoluidine (I), *p*-$C_6H_4Cl{\cdot}NH_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$; no reaction occurs with *o*-nitroarylamines. *p*-Nitrophenol yields coloured products, α-$C_{10}H_7{\cdot}NH_2$ gives iminonaphthathiazine dyes, and β-$C_{10}H_7{\cdot}NH_2$ gives ββ′-dinaphthazine; azo-compounds are not obtained in these cases. In addition to azo-compound the *substance*, (*o*-$C_6H_4Me{\cdot}N_2{\cdot}C_6H_3Me{\cdot}N{:})_2$, m.p. 201°, is obtained from (I). Compounds of the type $Hg(NH{\cdot}COR)_2$ are supposed to tautomerise as follows: $Hg(NH{\cdot}COR)_2 \rightleftharpoons R{\cdot}CO{\cdot}NH{\cdot}Hg{\cdot}O{\cdot}CR{:}NH \rightleftharpoons Hg(O{\cdot}CR{:}NH)_2$. R. T.

Effect of substituents on the germicidal activity of phenols. II. Alkyl derivatives of 2 : 4-dichlorophenol. S. L. Chien and L. Y. Yun. **III. Chlorinated hydroxyphenyl alkyl sulphides.** S. L. Chien and K. T. Chow (*J. Chinese Chem. Soc.*, 1939, **7**, 40—45, 46—51; cf. A., 1937, II, 239).—II. 2 : 4 : 1-$C_6H_3Cl_2{\cdot}OH$ (at just above m.p.) and Alk·COCl at 100° afford 2 : 4-dichlorophenyl acetate, b.p. 167—168°/80 mm., propionate, b.p. 148°/14 mm., *n-butyrate*, b.p. 161—163°/20 mm., and *n-valerate*, b.p. 172°/16 mm., which are rearranged by $AlCl_3$ at 170° to 3 : 5-*dichloro*-2-*hydroxy*-*acetophenone*, m.p. 95—96°, *-propiophenone*, m.p. 115—116°, *-butyrophenone*, m.p. 49—50°, and *-valerophenone*, m.p. 46—47°, respectively, reduced (Clemmensen) to 2 : 4-*dichloro*-6-*ethyl*-, b.p. 202—203°/22 mm., -n-*propyl*-, b.p. 136—137°/14 mm., -n-*butyl*-, b.p. 161—163°/11 mm., and -n-*amyl*-*phenol*, b.p. 165—167°/24 mm., respectively.

III. 4 : 2 : 1-$NH_2{\cdot}C_6H_3Cl{\cdot}OH$ (modified prep.) is converted (diazo-reaction and decomp. of xanthate ester by NaOH) into 3-*chloro*-4-*hydroxythiophenol*, m.p. 39—40°, which with RI in ROH–NaOH affords 3-*chloro*-4-*hydroxyphenyl Me*, b.p. 130—131°/10 mm., *Et*, b.p. 128—129°/8—9 mm., *Pr*$^{\alpha}$, b.p. 140—142°/10 mm., and *Bu*$^{\alpha}$ *sulphide*, b.p. 145—148°/8—10 mm. A. T. P.

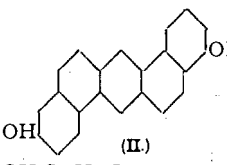
Organic molecular compounds. V. Formation of crystalline organic molecular compounds. C. Shinomiya (*Bull. Chem. Soc. Japan*, 1940, **15**, 309—314; cf. A., 1940, I, 412).—Data relating to the formation of cryst. mol. compounds having as one constituent α- or β-$C_{10}H_7{\cdot}OH$, α- or β-$C_{10}H_7{\cdot}NH_2$, or a derivative of *s*-$C_6H_3(NO_2)_3$ are tabulated and discussed with reference to the influence of configuration on compound formation. F. L. U.

Action of tyrosinase on quinol.—See A., 1941, III, 47.

Preparation of synthetic sex hormones. I. Hexœstrol. S. Bernstein and E. S. Wallis (*J. Amer. Chem. Soc.*, 1940, **62**, 2871—2873).—*p*-OMe·$C_6H_4{\cdot}COEt$ (prep. from the OH-ketone by Me_2SO_4–NaOH at 80°), b.p. 151—152°/19 mm., and Na–EtOH give *p*-OMe·$C_6H_4{\cdot}CHEt{\cdot}OH$ (60%), b.p. 137—140°/11·5 mm. (N_2), converted by gaseous HBr at 0° into the bromide, which (crude) with Na wire in Et_2O gives (*p*-OMe·$C_6H_4{\cdot}CHEt)_2$ (15%), m.p. 142—143·5°. Demethylation by AcOH–HI (*d* 1·7) at 135—140° gives 87% of (*p*-OH·$C_6H_4{\cdot}CHEt)_2$, m.p. 184—185°. R. S. C.

4 : 4′-Dihydroxy-αβ-diethylstilbene.—See B., 1940, 844.

Synthesis of 4′ : 8′-dihydroxy-1 : 2 : 5 : 6-dibenzanthracene. Its relation to products of metabolism of the hydrocarbon. J. Cason and L. F. Fieser (*J. Amer. Chem. Soc.*, 1940, **62**, 2681—2687).—1 : 2-Benzanthraquinone with 30% oleum at ~35° gives the 4′-sulphonic acid, best (94%) isolated as *p*-$C_6H_4Me{\cdot}NH_2$ salt, decomp. >300°, which affords (method of Sempronj, A., 1939, II, 514) 4′-hydroxy-1 : 2-benzanthracene, m.p. 231·5—232·5° (*loc. cit.*, 230°) [acetate, m.p. 195—195·5° (*loc. cit.*, 193—194°)]. Pyrolysis of crude 2 : 1-$C_{10}H_6Me{\cdot}CO{\cdot}C_{10}H_7$-2 at 430±5° gives 31% of 1 : 2 : 5 : 6-dibenzanthracene (I), m.p. 260—262°, oxidised by $Na_2Cr_2O_7$ (less well, CrO_3) in boiling AcOH to the quinone (79·5%), m.p. 244—249°. With 30% oleum at ≯35° this gives 1 : 2 : 5 : 6-dibenzanthraquinone-4′ : 8′-disulphonic acid (K_2 salt), isolated as (*p*-$C_6H_4Me{\cdot}NH_2)_2$ salt, which with Zn dust in aq. NH_3 at 85—90° gives Zn 1 : 2 : 5 : 6-dibenzanthracene-4′ : 8′-disulphonate, converted by KOH at 300—310° into 4′ : 8′-*dihydroxy*-1 : 2 : 5 : 6-*dibenzanthracene* (II), m.p. 415—418° (vac.), resolidifies, and then unmelted at >460° (vac.). $Na_2Cr_2O_7$ oxidises the *diacetate*, m.p. 360—362° (decomp.; vac.), thereof in boiling AcOH to the *quinone diacetate*, m.p. 340—345° (decomp.; vac.), which with KOH at 260° (later 280°) gives 5 : 2-OH·$C_{10}H_6{\cdot}CO_2H$ and with boiling KOH–EtOH gives 4′ : 8′-*dihydroxy*-1 : 2 : 5 : 6-*dibenzanthraquinone*, decomp. 370—375° (vac.). The rabbit-metabolism product from (I) (Levi *et al.*, *Chem. and Ind.*, 1937, 446) differs from (II), but the rat- and mice-metabolism product (Dobriner *et al.*, *Proc. Soc. Exp. Biol. Med.*, 1939, **41**, 67) is identical with (I). Metabolism and chemical substitution may thus occur at different points. M.p. are corr. R. S. C.


(II.)

Rearrangement of *o*-tolyl triphenylmethyl ether. Direct synthesis of 4-methoxy-3-methyltetraphenylmethane. H. A. Iddles and H. L. Minckler (*J. Amer. Chem. Soc.*, 1940, **62**, 2757—2759).—Rearrangement of *o*-$C_6H_4Me{\cdot}O{\cdot}CPh_3$ to 2 : 1 : 5-OH·$C_6H_3Me{\cdot}CPh_3$ is confirmed (cf. A., 1940, II, 12, 78). 2 : 1 : 5-OMe·$C_6H_3Me{\cdot}COPh$ (prep. from *o*-$C_6H_4Me{\cdot}OMe$ by BzCl and $SnCl_4$ in C_6H_6), m.p. 78°, with MgPhBr gives 80% of 4-*methoxy*-3-*methyltriphenylcarbinol* (I), m.p. 76·5°. 1 : 5 : 2-$C_6H_3MeBr{\cdot}OMe$ (prep. from the phenol by Me_2SO_4 and 33% NaOH at 40°), m.p. 66·5—67°, gives a Grignard reagent, which with $COPh_2$ in Et_2O gives 50% of (I). AcBr and (I) in light petroleum give the *bromide*, m.p. 106°, which with MgPhBr gives 4 : 3 : 1-OMe·$C_6H_3Me{\cdot}CPh_3$, m.p. 162° (Br-derivative, m.p. 185°) (cf. *locc. cit.*). R. S. C.

Trimethylquinol monophytyl ether.—See B., 1940, 897.

Derivatives of thymol. T. H. Tang and C. H. Chao (*J. Chem. Eng. China*, 1939, **6**, 23—26).—Aminothymol (I) heated with the acid chloride gives the *Bz*$_1$, m.p. 119—120°, and *cinnamoyl*, m.p. 231°, derivatives; BzCl and 10% NaOH at <25° afford the *Bz*$_2$ derivative, m.p. 164—165°. *Piperidyl-aminothymol*, m.p. 164—165° (previous darkening), is formed when (I) is heated with piperidine. *Salicylidene-* and *vanillylidene-aminothymol* have m.p. 170—171° and 197°, respectively. Contrary to Gilfillan *et al.* (cf. A., 1937, II, 14), nitrosothymol dissolves in saturated HCl to a colourless solution which turns red with alkali; a green colour is due to admixed, unknown, oily impurity. H. B.

Thiol and cysteine derivatives of 1 : 2-benzanthracene, 10-methyl-1 : 2-benzanthracene, and 3 : 4-benzpyrene. J. L. Wood and L. F. Fieser (*J. Amer. Chem. Soc.*, 1940, **62**, 2674—2681).—The cysteine derivatives described below are unstable and may not persist as such during tests for carcinogenic activity. S_2Cl_2 and 1 : 2-benzanthracene (after an induction period, if pure), best in light petroleum, give a product converted by molten Na_2S,H_2O at 130° into 10-*thiol*-1 : 2-*benzanthracene* (I), dimorphic, m.p. 115° (instantaneous), resolidifying with m.p. 138°, and 139·9—140·7°, sublimes at 130°/1 mm. (S-CH_2Ph derivative, m.p. 128·2—129·4°), also obtained from the Grignard reagent of 10-bromo-1 : 2-benzanthracene (II) by S in C_6H_6. Oxidation of (I) by $Na_2Cr_2O_7$–AcOH at 60° gives 1 : 2-benzanthraquinone and by O_2 in NaOH–aq. dioxan containing a trace of $FeCl_3$ gives *di*-1 : 2-*benz*-10-*anthranyl disulphide* (III), m.p. 208·2—209·7° (decomp.; vac.). (II) is converted into 1 : 2-benzanthracene by KSH in 95% EtOH at 180°. Gradual addition of equiv. amounts of aq. NaOH and *dl*-$CH_2Cl{\cdot}CH(CO_2H){\cdot}NH_2,HCl$ to the Na salt of (I) in aq. dioxan–N_2 gives 25% of S-1 : 2-*benz*-10-*anthranylcysteine*, decomp. 192—194° (yellow at 187°) [converted into (III) in boiling dioxan], and (III). 3 : 4-Benzpyrene and S_2Cl_2 in light petroleum (as above) or 5-chloro-3 : 4-benzpyrene and KSH in 95% EtOH at 150° give 5-*thiol*-3 : 4-*benzpyrene*, decomp. 205—206° (197—198·5°) [S-CH_2Ph derivative, decomp. 170·2—172·2°; derived *disulphide* (IV), m.p. 271—272° (decomp.; vac.)], and thence as above S-3 : 4-*benz*-5-*pyrenylcysteine*, decomp. 146·7—147·5° (varies with rate of heating), and (IV). 10-Chloromethyl-1 : 2-benzanthracene (V), m.p. 190—190·6°, and $CS(NH_2)_2$ in boiling abs. EtOH give 86% of S-1 : 2-

benz-10-*anthranylmethylisothiocarbamide*, m.p. 160° (instantaneous), resolidifies, m.p. >235° [*hydrochloride*, m.p. 213—214° (decomp.)], which with Na_2CO_3 and a trace of $Na_2S_2O_4$ in boiling H_2O–MeOH gives 10-*thiolmethyl*-1 : 2-*benzanthracene*, m.p. 172·7—174·7° (S-CH_2Ph derivative, m.p. 150·2—150·6°). The derived *disulphide* (**VI**) has m.p. 244·5—245° (decomp.; vac.). 10-Methyl-1 : 2-benzanthracene [prep. from (**V**) by $SnCl_2$ and conc. HCl in dioxan at room temp. and later 100°] and S_2Cl_2 in hexane give, after an induction period, a crude mercaptan, whence oxidation yields some (**VI**). Reduction of *l*-cystine by Na in liquid NH_3 and subsequent addition of NH_4Cl, PhMe, and (**V**) gives S-1 : 2-*benzanthranylmethyl*-l-*cysteine*, decomp. 205·7—206·7° (bath preheated at 205°), $[\alpha]_D^{23}$ −7·5° in dioxan–2N-HCl (2 : 1). M.p. are corr. R. S. C.

Retropinacolin rearrangement of 10 : 10-diaryl-9 : 10-dihydro-9-phenanthrols. (Miss) E. J. H. Chu and F. Wei (*J. Chinese Chem. Soc.*, 1939, **7**, 20—23; cf. A., 1935, 973; Bachmann, A., 1933, 1159).—10 : 10-Di-*p*-phenetyl- or -*p*-chlorophenyl-9-phenanthrone and Zn dust–NaOH–EtOH or (better) $MgPr^{\beta}Br$–Et_2O–C_6H_6 give 10 : 10-*di*-p-*phenetyl*- (**I**), m.p. 146·2°, or -p-*chlorophenyl*-9 : 10-*dihydro*-9-*phenanthrol* (**II**), m.p. 159·3°, respectively, reoxidised by CrO_3–AcOH to the corresponding phenanthrone. (**I**) and (**II**) are converted quantitatively by I–AcOH into 9 : 10-*di*-p-*phenetyl*-, m.p. 207°, and -p-*chlorophenyl*-*phenanthrene*, m.p. 244°, respectively, oxidised by CrO_3–AcOH to the corresponding 2 : 2′-diaroyldiphenyl. A. T. P.

Reactions of 2 : 2′-diacyldiphenyls. I. Reaction between 2 : 2′-diacyldiphenyls and magnesium ethyl bromide. (Miss) E. J. H. Chu (*J. Chinese Chem. Soc.*, 1939, **7**, 24—26).—2 : 2′-Dibenzoyldiphenyl and MgEtBr afford 2 : 2′-*di*-(α-*hydroxy*-α-*phenylpropyl*)*diphenyl*, m.p. 221·7—222·7°. Similarly prepared are 2 : 2′-*di*-(α-*hydroxy*-α-p-*diphenylyl*-, m.p. 183·6—184·6°, -p-*phenetyl*-, m.p. 135—136°, -m-*tolyl*-, m.p. 156·3—157·3°, and -p-*chlorophenyl*-*propyl*)*diphenyl*, m.p. 228·5—229·5°. A. T. P.

Sterols. CVIII. Preparation of dihydroandrosterone and related compounds from diosgenin and tigogenin. R. E. Marker (*J. Amer. Chem. Soc.*, 1940, **62**, 2621—2625).—Tigogenone (**I**) [prep. from diosgenin by way of tigogenin (**II**)] and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give (**II**) (separated as digitonide) and epi*tigogenin* (**III**), m.p. 242—245° [*acetate*, m.p. 199—202°; oxidised to (**I**)], which with Ac_2O at 200° gives ψ-epi*tigogenin* (**IV**), m.p. 148—150°, reconverted into (**III**) by conc. HCl–EtOH and oxidised by CrO_3–AcOH at 25° to Δ^{16}-*allo*pregnene-3 : 20-dione (**V**). Oxidation of the crude acetate of (**IV**) and subsequent hydrolysis gives Δ^{16}-allo*pregnen*-3(α)-*ol*-20-*one* (**VI**), m.p. 219—222° [*acetate* (**VII**), m.p. 156—158°], reduced (H_2–Pd–$BaSO_4$; EtOH–Et_2O; 1·5 atm.) to *allo*pregnan-3(α)-ol-20-one, m.p. 172—174° [acetate (**VIII**), m.p. 138—140°, obtained also by hydrogenation of (**VII**)]. With Caro's acid in AcOH, (**VIII**) gives a mixture, whence removal of ketones by Girard's reagent and hydrolysis yields androstane-3(α) : 17(α)-diol, m.p. 219—222° (diacetate, m.p. 160—162°). H_2–PtO_2 at 3 atm. converts (**IV**) in AcOH into *dihydro*-ψ-epi*tigogenin*, m.p. 193—196° [oxidised to (**V**)], the *diacetate*, m.p. 118—121°, of which with CrO_3–AcOH gives (**VI**). R. S. C.

Photodehydrogenation of sterols. I. $\Delta^{2:4}$-Cholestadiene. R. P. Jacobsen and C. Z. Nawrocki (*J. Amer. Chem. Soc.*, 1940, **62**, 2612—2614).—Irradiation (W) of ergosterol in C_6H_6 containing a little EtOH and mixed halogenofluoresceins gives 61—64% of diergostatrienol, m.p. 198—199° (decomp.) [general absorption at <2900 A.; *diacetate*, m.p. 201—202° (decomp.)]. Dehydroergosterol in presence of rose-Bengal in EtOH gives 50% of diergostatetraenol (50%), m.p. 194—195° (decomp.), absorption max. at 2650 A. (log ε 3·95). $\Delta^{2:4}$-Cholestadiene gives similarly a very small yield of a *dicholestadiene*, m.p. 203—204° (decomp.) (general absorption at <2600 A.). M.p. are corr. R. S. C.

Alkylation of cyanophenylpyruvic ester. G. S. Skinner and A. J. Green (*J. Amer. Chem. Soc.*, 1940, **62**, 2882).—CN·CHPh·CO·CO_2Me with CH_2:CH·CH_2Br or CH_2PhCl and NaOEt–EtOH at 0° and then 70° gives α-*phenyl*-Δ$^{\gamma}$-*pentenonitrile*, b.p. 134—135°/16 mm., and αβ-*diphenylpropionitrile*, m.p. 52—53°, b.p. 159—160°/6 mm., respectively, but with Me_2SO_4 or Et_2SO_4 and NaOEt–EtOH gives *Me* α-*keto*-β-*cyano*-β-*phenyl*-n-*butyrate*, b.p. 148—150°/2 mm., and -n-*valerate*, b.p. 161—162°/5 mm., respectively. R. S. C.

γγ′-Di-*p*-tolyl-γγ′-suberodilactone. C. C. Price (*J. Amer. Chem. Soc.*, 1940, **62**, 2884—2885).—*p*-C_6H_4Me·CO·$[CH_2]_2$·CO_2H and Zn dust in boiling 80% AcOH give γ-*p*-tolyl-γ-butyrolactone, m.p. 67—68° (lit. 69°), and a little γγ′-*di*-p-*tolyl*-γγ′-*suberodilactone*, m.p. 275—276°. R. S. C.

Action of diazobenzene on alkylacetoacetic ester as method of preparing α-amino-acids and phenylhydrazones of α-keto-acids. II. Synthesis of phenylalanine. IV. Synthesis of the phenylhydrazone of phenylpyruvic acid. V. V. Feofilaktov and E. Vinogradova (*J. Gen. Chem. Russ.*, 1940, **10**, 255—257, 260—262).—An account of work already noted (A., 1940, II, 70, 85).

Synthesis of 2-, 4-, and 9-fluorenylacetic acid. W. E. Bachmann and J. C. Sheehan (*J. Amer. Chem. Soc.*, 1940, **62**, 2687—2690).—2-Acetylfluorene (prep. from fluorene, Ac_2O, and $AlCl_3$ in $PhNO_2$ at, successively, −5°, 0°, and room temp.), m.p. 128—129° (lit., 132°), and NH_4 polysulphide in dioxan at 160° give 2-*fluorenylacetamide* (70%), m.p. 264—266° (slight decomp.), hydrolysed by boiling, HCl–AcOH to 2-fluorenylacetic acid, m.p. 186—187° (lit. 178°), sublimes at 170°/0·01 mm., also obtained (32%) by the Arndt–Eistert reaction from fluorene-2-carboxylic acid. Fluorenone-4-carboxylic acid and Zn dust in aq. NaOH–PhMe give 9-hydroxyfluorene-4-carboxylic acid (85%), reduced (92%) by red P–I–AcOH–H_2O to fluorene-4-carboxylic acid, which gives (Arndt–Eistert) 4-*fluorenylacetic acid* (**I**) (89%), m.p. 178·5—179°. 4-*Fluorenonylacetic acid*, m.p. 206—207° after softening, sublimes at 180°/0·01 mm. (*Me* ester, m.p. 135·5—136°, sublimes at 0·01 mm.), is obtained from the 4-carboxylic acid by the Arndt–Eistert reaction and is reduced to (**I**) by Zn–NaOH, followed by HI. 9-Bromofluorene (prep. from fluorenol by AcBr), m.p. 102—103°, gives by $CH_2(CO_2Et)_2$ etc. 9-fluorenylacetic acid (89%), m.p. 131·5—132·5° (lit., 128—129°, 137° 138—139°), b.p. 170°/0·01 mm. R. S. C.

Tertiary naphthenic acids. I. Synthesis of 1 : 2 : 3 : 3-tetramethyl*cyclo*pentane-1-carboxylic acid from camphor. B. Shive, J. T. Horeczy, and H. L. Lochte (*J. Amer. Chem. Soc.*, 1940, **62**, 2744—2746).—*iso*Lauronolic acid (modified prep.) and H_2–Raney Ni in dioxan at 175°/4500 lb. or (slowly) H_2–PtO_2–AcOH at 1·5 atm. give the H_2-acid (amide, new m.p. 164°; *anilide*, m.p. 156—157°), the chloride, b.p. 201°/746 mm., of which with C_6H_6 and $AlCl_3$ gives 3-*benzoyl*-1 : 1 : 2-*trimethyl*cyclo*pentane*, b.p. 299°/751 mm. (*oxime*, m.p. 105—106°). $NaNH_2$–C_6H_6 and then MeI in PhMe give 3-*benzoyl*-1 : 1 : 2 : 3-*tetramethyl*cyclo*pentane*, b.p. 307—308°/750 mm. (*oxime*, m.p. 154—155°), oxidised by O_3 in CCl_4 followed by alkaline H_2O_2 to 1 : 2 : 3 : 3-*tetramethyl*-cyclo*pentane*-1-*carboxylic acid* (**I**), m.p. 125—126°, and converted by $NaNH_2$ into (**I**) and its *amide*, m.p. 85—86°. (**I**) is not identical with the acid obtained from Californian petroleum by Horeczy *et al.* (cf. Roberts *et al.*) (both unpublished). R. S. C.

Esters of brominated aminobenzoic acids. M. B. Moore and E. H. Volwiler (*J. Amer. Chem. Soc.*, 1940, **62**, 2799—2801).—3 : 2 : 1-NO_2·C_6H_3Br·CO_2K, Br·$[CH_2]_2$·Br, and a trace of $NHEt_2$ at ~140° give γ-*bromo*-n-*propyl* 2-*bromo*-3-*nitrobenzoate*, an oil, which with $NHBu^{\alpha}_2$ gives the γ-di-*n*-butylamino-*n*-propyl ester, the hygroscopic hydrochloride of which is reduced by Fe to γ-di-*n*-butylamino-*n*-propyl 2-bromo-3-aminobenzoate (*hydriodide*, m.p. 160—161°). 4 : 2 : 1-NO_2·C_6H_3Br·CO_2H leads by similar reactions to γ-*di*-n-*butylamino*-n-*propyl* 2-*bromo*-4-*aminobenzoate hydriodide*, m.p. 149—150°. Passage of Br vapour into procaine hydrochloride in H_2O or, better, interaction of procaine with Br–$CHCl_3$ gives β-diethylaminoethyl 3-bromo-4-aminobenzoate {hydrochloride, m.p. 154—155° [lit. (+H_2O) 157—158°]; *hydrobromide*, m.p. 165—166°}. *p*-NH_2·C_6H_4·CO_2·$[CH_2]_3$·NBu^{α}_2 (**I**) and Br–AcOH at room temp. give γ-di-*n*-butylamino-*n*-propyl 3-bromo-4-aminobenzoate (*acetate*, m.p. 71—72°; hydrobromide, m.p. 129—130°), which with $Pr^{\alpha}Br$ in boiling $Pr^{\alpha}OH$ gives the 3-bromo-4-*n*-propylaminobenzoate (*hydrochloride*, m.p. 146—148°). (**I**) and Br–$CHCl_3$ at room temp. give γ-*di*-n-*butylamino*-n-*propyl* 3 : 5-*dibromo*-4-*aminobenzoate hydrobromide*, m.p. 162·5—163°. Alkylation (as above) leads to γ-*di*-n-*butylamino*-n-*propyl* 3-*bromo*-4-n-*butyl*-, m.p. 116—117°, 2-*bromo*-3-n-*butyl*-, m.p. 169—171°, and 3 : 5-*dibromo*-4-n-*propyl*-, m.p. 117—118°, -*aminobenzoate hydrochloride*. The monobromoamino-esters are anæsthetics, the salts of which are inconveniently insol. The dibromoamino-esters are mainly convulsant. R. S. C.

Chloralamides. II. Chloral-nitro- and -bromo-salicylamide. N. W. Hirwe, (Miss) K. D. Gavankar, and B. V. Patil (*Proc. Indian Acad. Sci.*, 1940, **11**, **A**, 512—516).—Chloralsalicylamide (**I**) with HNO_3 (*d* 1·2) at room temp. for 4 days gives *chloral-3-nitrosalicylamide* (**II**), m.p. 154° [*Na*$_2$, *K*$_2$, and *Ca* salt (+5H$_2$O)], with some 5-nitrosalicylamide, m.p. 224—225°. (**II**) is also obtained from 3-nitrosalicylamide and chloral (**III**), which with 5-bromo-3-nitrosalicylamide (**IV**) gives *chloral-5-bromo-3-nitrosalicylamide*, m.p. 155° (decomp.). Bromination of (**II**) in AcOH gives (**IV**). In conc. H_2SO_4–HNO_3 (*d* 1·45), (**I**) gives *chloral-3 : 5-dinitrosalicylamide*, m.p. 154° (decomp.), whilst chloral-2-methoxybenzamide (**V**) gives *chloral-5-nitro-*, m.p. 155° (decomp.), or -3 : 5-*dinitro-2-methoxybenzamide*, m.p. 142—143° (decomp.), according to the conditions used. In AcOH with Br vapour, (**I**) gives *chloral-5-bromo-* (**VI**), m.p. 150—152°, and, in presence of I, -3 : 5-*dibromo-salicylamide*, m.p. 158—160°, whilst (**V**) gives *chloral-5-bromo-2-methoxybenzamide*, m.p. 147—148°. These compounds [except (**VI**)] are also synthesised from (**III**), which also yields *chloral-3-bromosalicylamide*, m.p. 161°, and -3-*bromo-*, m.p. 129°, -3 : 5-*dibromo-*, m.p. 156°, and -3-*nitro-2-methoxybenzamide*, m.p. 106° (decomp.). E. W. W.

Chloralamides. Action of potassium cyanide on α-chloro-chloral-chloro- and -bromo-2-methoxybenzamides and hydrolysis of the resulting α-cyano-compounds. N. W. Hirwe and K. N. Rana (*J. Indian Chem. Soc.*, 1940, **17**, 481—484; cf. A., 1940, II, 220).—α-Chlorochloral-5-chloro-2-methoxybenzamide [5-chloro-2-methoxybenz-αβββ-tetrachloroethylamide] and KCN–$COMe_2$ afford N-*ββ-dichloro-α-cyano-*, m.p. 171—172° (yield, ~39%), and thence [conc. HCl at 100° (bath)] N-*ββ-dichloro-α-carboxy-vinyl-5-chloro-2-methoxybenzamide*, m.p. 199—200° (decomp.) [*Na* and *Ba* (+2H$_2$O) salts] (high yield). Similarly prepared are N-*ββ-dichloro-α-cyanovinyl-3 : 5-dichloro-*, m.p. 172—173°, -5-*bromo-*, m.p. 177—178°, and -3 : 5-*dibromo-2-methoxybenzamide*, m.p. 220—221° (decomp.), and N-*ββ-dichloro-α-carboxyvinyl-3 : 5-dichloro-*, m.p. 202—203° (decomp.) [*Na* (+H$_2$O) and *Ba* (+4H$_2$O) salts], -5-*bromo-*, m.p. 203—204° (decomp.) [*Na* and *Ca* (+2H$_2$O) salts], and -3 : 5-*dibromo-2-methoxybenzamide*, m.p. 217—218° (decomp.) [*Na* (+2H$_2$O) and *Ba* (+3H$_2$O) salts]. A. T. P.

Phenylthiocarbamides. The triad –N·C·S–. IX. Thiobenzamide. H. Krall and V. Sagar (*J. Indian Chem. Soc.*, 1940, **17**, 475—479; cf. A., 1938, **II**, 358).—Thiobenzamide (**I**) yields with N-KOH (1 equiv.), H_2S (67%), PhCN, and a trace of NH_3, and with N-HCl (1 equiv.), H_2S (9·5%), NH_3 (10%), and BzOH. The latter reaction occurs to 2% in neutral solution. HNO_2 with (**I**) yields, in presence of HCl, NO (79%) and dibenzenylazosulphime (von Hofmann *et al.*, A., 1892, 1109), and in presence of AcOH, N_2 (38%) and NO (62%). It is concluded that in neutral solution (**I**) contains 40% of the form CSPh·NH$_2$; acids and alkalis effect almost complete rearrangement to the form NH:CPh·SH. A. Li.

Colour in relation to chemical constitution of the phthalein dyes. Phthaleins of mixed type. S. Dutt (*Proc. Indian Acad. Sci.*, 1940, **11**, **A**, 483—490).—Unsymmetrical phthaleins obtained from *o*-C$_6$H$_4$Bz·CO$_2$H and phenols and aminophenols have much less intense colour in alkaline solution than have the symmetrical phthaleins from *o*-C$_6$H$_4$(CO$_2$H)$_2$; this is ascribed to less intense (because unidirectional) tautomerism in the former between lactonoid and quinonoid forms. In some compounds, hot alkali is needed to develop colour. The *p*-hydroxydiphenylphthalein (phenylphenolphthalein) obtained by Pechmann (A., 1881, 96) was heavily contaminated with phenolphthalein; the pure compound has new m.p. 92·5° and gives a light yellow solution (max. absorption at 4450 A.) in dil. NaOH. The following are prepared (colours in dil. NaOH and absorption max.): *phenyl-o-*, m.p. 133° (light yellow; 4510 A.), and -m-*cresol-*, m.p. 146° (light yellow in hot NaOH; 4450 A.); *phenyl-carvacrol-*, m.p. 236°, and -*thymol-*, m.p. 253° (both deep yellow in hot NaOH; 4480 A.); -*resorcinol-*, m.p. 169° (orange yellow; 4710 A.); -*pyrocatechol-*, m.p. 86° (red; 5330 A.); -*quinol-*, m.p. 241° (deep yellow; 4565 A.); -α-*naphthol-*, m.p. 229° (deep yellow; 4900 A.); -*phloroglucinol-*, m.p. 117° (deep yellow; 4650 A.); -*pyrogallol-*, m.p. 126° (deep yellow; 4725 A.); and -m-*dimethylaminophenol-phthalein*, m.p. 124°, and its *hydrochloride*, m.p. 102° (pink in EtOH and H_2O respectively; 5550 A.). E. W. W.

8-Amino-1-naphthoic acid.—See B., 1940, 845.

Reaction of substituted phenanthrenes with lithium *n*-butyl. H. Gilman and T. H. Cook (*J. Amer. Chem. Soc.*, 1940, **62**, 2813—2817).—2-, 3-, and 9-Bromophenanthrene with LiBu^a in Et_2O–N_2, followed by CO_2, give the 2- (37%), 3- (32%), and 9-carboxylic acid (51%), respectively. 2-Hydroxyphenanthrene gives 2-*hydroxyphenanthrene-3-carboxylic acid* (1·5%), m.p. 276—277° after sintering [*Me ether* (**I**), m.p. 211—213° (Me ester, dimorphic, m.p. 77—78° and 94—95°)]. 2-Methoxyphenanthrene gives a Li derivative, converted by CO_2 into (**I**) (39%) and by air in presence of MgBu^{a}Br into 3-*hydroxy-2-methoxyphenanthrene* (18·5%), m.p. 145—146° (*acetate*, m.p. 146—147°) (and other products), which with Me_2SO_4–50% KOH–$COMe_2$ gives 2 : 3-dimethoxyphenanthrene (**II**). 3-Hydroxyphenanthrene is metalated with difficulty. 3-Methoxyphenanthrene gives the 2-Li derivative, converted as above into 3-*methoxyphenanthrene-2-carboxylic acid* (33%), m.p. 185° (Me ester, m.p. 134—134·5°), and 2-*hydroxy-3-methoxyphenanthrene* (30%), m.p. 171—172° [Me ether = (**II**); *acetate*, m.p. 142—144°]. 9-Hydroxyphenanthrene gives a Li derivative, converted by CO_2 into 9-*hydroxyphenanthrene-x-carboxylic acid*, m.p. 158—160° (decomp.) [*Me ether* (**III**), m.p. 197—199°], and by Br into a little of a compound, m.p. 124—124·5°, which with CrO_3–AcOH gives phenanthraquinone. 9-Methoxyphenanthrene gives a Li derivative, converted by CO_2 into the 10-carboxylic acid and (**III**), and by O_2–MgBu^{a}Br into (?) 10-*hydroxy-9-methoxyphenanthrene*, m.p. 94—95·5°. R. S. C.

Cyclic *o*-dinitriles.—See B., 1940, 845.

Influence of substitution on the formation of derivatives of α-hydrindone and 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. Synthesis of 1 : 2 : 3 : 4-tetrahydronaphthalene-1 : 2-dicarboxylic acid. N. N. Chatterjee and G. N. Barpujari (*J. Indian Chem. Soc.*, 1940, **17**, 292—296).—Successive treatments of CN·CHNa·CO$_2$Et in EtOH with OH·CHPh·CN and CH$_2$Cl·CO$_2$Et give *Et*$_2$ *αβ-dicyano-α-phenyl-n-propane-βγ-dicarboxylate*, b.p. 205—207°/4 mm., hydrolysed by boiling 70% H_2SO_4 to α-phenyl-*n*-propane-*αβγ*-tricarboxylic acid, m.p. 204° (*Et*$_3$ ester, b.p. 185—190°/5 mm.), which with H_2SO_4 (*d* 1·84) at 100° affords 1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene-3 : 4-dicarboxylic acid* (**I**), m.p. 179—182°, oxidised by alkaline $KMnO_4$ to *o*-C$_6$H$_4$(CO$_2$H)$_2$. Clemmensen reduction of (**I**) gives 1 : 2 : 3 : 4-tetrahydronaphthalene-1 : 2-dicarboxylic acid, m.p. 193° when rapidly heated. Similarly *p*-OMe·C$_6$H$_4$·CH(OH)·CN (**II**) affords *Et*$_2$ *αβ-dicyano-α-p-anisyl-n-propane-βγ-dicarboxylate*, b.p. 232—237°/3 mm., which gives α-p-*anisyl*-n-*propane-αβγ-tricarboxylic acid*, m.p. 190° when rapidly heated (*Et*$_3$ ester, b.p. 210—215°/5 mm.), which is sulphonated and not cyclised by H_2SO_4. Condensation of (**II**) with CN·CHNa·CO$_2$Et gives *Et αβ-dicyano-β-p-anisylpropionate*, b.p. 225°/5 mm., m.p. 81°, hydrolysed by boiling dil. H_2SO_4 to *p*-anisylsuccinic acid, m.p. 205° (anhydride, m.p. 91°; *Et*$_2$ ester, b.p. 185°/4 mm.). H. W.

Reactions of keten with salicylaldehyde and *p*-hydroxybenzaldehyde. J. W. Williams and A. Sadle (*J. Amer. Chem. Soc.*, 1940, **62**, 2801—2803).—Pure *o*-OH·C$_6$H$_4$·CHO (**I**) and keten at room temp. give 84% of *o*-OAc·C$_6$H$_4$·CHO (**II**) and 9% of coumarin (**III**). In presence of a drop of H_2SO_4 31% of (**III**) is obtained. With anhyd. NaOAc in $COMe_2$ 1—2% of *o*-OAc·C$_6$H$_4$·CH:CH·CO$_2$H (**IV**) is formed. In presence of H_2SO_4, keten and (**II**) give only 2—5% of (**III**). Possible reaction mechanisms are discussed. When boiled alone, (**II**) gives slowly a little (**III**), the amount being slightly increased by presence of a drop of H_2SO_4; presence of anhyd. NaOAc leads to (**III**) and (**I**); in all cases AcOH and Ac_2O are formed from liberated keten. *p*-OH·C$_6$H$_4$·CHO and keten in $COMe_2$ at room temp. give 91% of *p*-OAc·C$_6$H$_4$·CHO (**V**) (oxidised by air), but presence of anhyd. NaOAc leads to 5% of *p*-OAc·C$_6$H$_4$·CH:CH·CO$_2$H, also obtained in 6% yield similarly from (**V**). The *p*-OAc-compounds are hydrolysed by cold 10% aq. NaOH. R. S. C.

Acenaphthene series. I. 3-Benzoylacenaphthene and related compounds. (Miss) E. J. H. Chu (*J. Chinese Chem. Soc.*, 1939, **7**, 14—19).—3-Benzoylacenaphthene (**I**) (improved prep.) affords a mixture, m.p. 175—183°, of oximes [one has m.p. 184° (decomp.); cf. Graebe *et al.*, A., 1903, i, 409], converted by PhSO$_2$Cl–C$_5$H$_5$N or by PCl$_5$–C$_6$H$_6$ into a mixture of 3-acenaphthanilide and 3-benzamidoacenaphthene [one has m.p. 178·5—179·5° (decomp.), the other m.p. 213—213·5° (decomp.)], hydrolysed (boiling KOH–EtOH for 3 days) to the respective acids. (**I**) and MgPhBr afford *diphenyl-*

3-*acenaphthylcarbinol*, m.p. 200·8° (decomp.). (I) is reduced (modified Clemmensen) to 3-benzylacenaphthene or (by Zn dust–NaOH–EtOH) to phenyl-3-acenaphthylcarbinol.

A. T. P.

Cyclisation of dieninenes. IX. Synthesis of a new perhydrophenanthr-9-one. C. S. Marvel and R. V. White. **X. Dodecahydrophenanthrone obtained from di*cyclo*hexenylacetylene.** C. S. Marvel, D. E. Pearson, and R. V. White (*J. Amer. Chem. Soc.*, 1940, **62**, 2739—2740, 2741—2743; cf. below).—IX. 9-Hydroxyphenanthrene and H_2–Raney Ni–EtOH at 150°/267 atm. give 9-*hydroxytetradecahydrophenanthrene* (44%), m.p. 66·5—67·5°, b.p. 115—120°/3·5 mm., oxidised by CrO_3–AcOH at room temp. to 9-*ketotetradecahydrophenanthrene*, m.p. 56—57°, b.p. 110—115°/3·5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 232—233°; *oxime*, m.p. 210—212°). HNO_3 then gives *dodecahydrodiphenic acid*, m.p. 174—175° (*anhydride*, m.p. 103—104°, not cyclised at 250—350°).

X. Crude 9-keto-$\Delta^{13:14}$-dodecahydrophenanthrene (I) (Linstead *et al.*, A., 1939, II, 307), purified by boiling with Zn dust in AcOH, then has m.p. 37° (*loc. cit.*, 39°), b.p. 113—115°/1·5 mm., and gives an oxime, m.p. 186° (lit. 183—184°); the non-cryst. portion, b.p. 117—118°/1·5 mm., gives an oxime, m.p. 124·5—126·5°. Crude (I) is hydrogenated (Pd) to 9-ketotetradecahydrophenanthrene (II), m.p. 47—48° (lit. 51°), which with Br–$CHCl_3$ gives the (? 14-)Br-derivative, b.p. 125—126°/1·5 mm., reconverted into (I) by boiling C_5H_5N. Dibromination of (II) and subsequent treatment with C_5H_5N gives a *compound*, $C_{14}H_{15}OBr$, m.p. 186—188°, containing an aromatic ring. Bromination of liquid 9-ketotetradecahydrophenanthrene, b.p. 116—118°/1·5 mm. (oxime, m.p. 137—142°), and then treatment with C_5H_5N gives (I), identified as oxime. MgMeBr and MgEtBr convert (I) into impure 9-hydroxy-9-methyl-, b.p. 94—96°/1 mm., and -ethyl-$\Delta^{13:14}$-dodecahydrophenanthrene, dehydrated by $KHSO_4$ at 150°/16 mm. to *hydrocarbons*, $C_{15}H_{22}$, b.p. 78—80°/1 mm., and $C_{16}H_{24}$, b.p. 117—118°/2 mm., which with Pd–C at 320° give 9-methyl-, m.p. 91—92° (picrate, new m.p. 154—155°), and nearly pure 9-ethyl-phenanthrene, respectively. MgPhBr and (I) give a *hydrocarbon*, $C_{20}H_{24}$, b.p. 138—140°/1 mm., dehydrogenated (Pt–C, CO_2, 320°) to (?) 9-*phenyloctahydrophenanthrene*, m.p. 95·5—96°. The structure of (I) is thus confirmed.

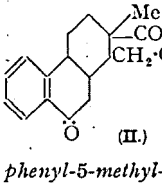
R. S. C.

Cyclisation of dieninenes. VIII. Ring-closures with α- and β-*cyclo*hexenylacetylene derivatives of octahydronaphthalene. C. S. Marvel, D. E. Pearson, and L. A. Patterson (*J. Amer. Chem. Soc.*, 1940, **62**, 2659—2665; cf. A., 1939, II, 499).—Mixed *cis*- and *trans*-1-ketodecahydronaphthalene, C_2H_2, and $CMe_2Et{\cdot}OK$–$CMe_2Et{\cdot}OH$–Et_2O give mixed cis- and trans-1-*hydroxy*-1-*acetylenyldecahydronaphthalene* (J), b.p. 74—76°/1·5 mm., which with first MgEtBr and then *cyclo*hexanone gives mixed α-1-*hydroxy*cyclo*hexyl*-β-1′-*hydroxydecahydro*-1′-*naphthylacetylene*, b.p. 186—194°/3 mm., dehydrated by $KHSO_4$ to α-Δ^1-cyclo*hexenyl*-β-$\Delta^{1'}$-*octahydro*-1′-*naphthylacetylene*, b.p. 156—162°/3 mm. Cyclisation by H_2SO_4–AcOH at 0° then gives 2-*keto*-$\Delta^{2a:6a}$-*hexadecahydrochrysene* (II), m.p. 103·5—104° (2 : 4-*dinitrophenylhydrazone*, m.p. 200°), and (?) 1-$\Delta^{1'}$-*octahydro*-1′-*naphthyl*-Δ^1-*hexahydrocoumarone* (III), b.p. 144—150°/3 mm. Zn–Hg–HCl–AcOH–PhMe reduces (II) to $\Delta^{2a:6a}$-*hexadecahydrochrysene*, b.p. 141—143°/3 mm., which with Pt–C in CO_2, first at 315° and then at 340°, gives chrysene, similarly obtained from (II) by Pt–C in CO_2 but only impure by S. H_2–Raney Ni in EtOH at 150°/200 atm. reduces (II) to the saturated alcohol, which with CrO_3–AcOH gives 2-keto-octadecahydrochrysene, m.p. 109·5—110°, b.p. 150—156°/1·5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 197—198°). With MgMeI in Et_2O–C_6H_6, this gives a carbinol, b.p. 142—147°/1·5 mm., dehydrogenated and dehydrated by Pt-black on asbestos in CO_2 at 320° to 2-methylchrysene, m.p. 160—161° [picrate, m.p. 171—172° (lit. 170°)]. In presence of Raney Ni at 160°/267 atm. (III) absorbs ~2 H_2 to give a compound, b.p. 123—130°/1·5 mm., whence Pt-black yields chrysene. With HBr in boiling AcOH, (III) gives a substance, $C_{18}H_{28}O$, b.p. 166—170°/2 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 198°). *trans*- and *cis*-2-Ketodecahydronaphthalene, respectively, give *trans*-, m.p. 94—94·5° (lit. 91·5°), b.p. 85—89°/15 mm., and cis-2-*hydroxy*-2-*acetylenyldecahydronaphthalene*, b.p. 90—94°/2 mm., trans-, m.p. 133°, and cis-α-1-*hydroxy*cyclo*hexyl*-β-2′-*hydroxydecahydro*-2′-*naphthylacetylene*, b.p. 178—184°/3 mm., and α-Δ^1-cyclo*hexenyl*-β-trans- (IV), b.p. 152—156°/3 mm., and -cis-(? $\Delta^{2'}$)-*octahydro*-2′-*naphthylacetylene* (V), b.p. 132—140°/3 mm. Cyclisation of (IV) gives an oil, converted by Zn–AcOH into $\Delta^{1:2}$-*hexadecahydro*-1 : 2-*benzanthr*-3-*one* (VI), m.p. 59—60° (2 : 4-*dinitrophenylhydrazone*, m.p 252—253°), and a *by-product*, b.p. 151—152°/1·5 mm. [with HBr–AcOH gives a product, $C_{18}H_{28}O$, b.p. 151—156°/1·5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 225°)]. (V) gives similarly a $\Delta^{1:2}$-*hexadecahydro*-1 : 2-*benzanthr*-3-*one* (VII), b.p. 158—165°/3 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 150—153°), and a by-product, b.p. 155—158°/3 mm. Clemmensen–Martin reduction and then Pt-black dehydrogenation of (VI) and (VII) gives 1 : 2-benzanthracene. Attempts to prepare a methylcarbinol etc. failed. The MgBr derivative of (I) and 1-ketodecahydronaphthalene give αβ-di-1-hydroxydecahydro-1-naphthylacetylene, an oil, and thence ($KHSO_4$) αβ-*di*-Δ^1-*octahydro*-1-*naphthylacetylene*, b.p. 176—180°/? 3 mm., which with H_2SO_4–AcOH–C_6H_6 gives a non-ketonic substance, b.p. 178—181°/1 mm., whence Pd-black–asbestos–CO_2 affords a little picene and HBr–AcOH gives a *substance*, $C_{22}H_{32}O$, b.p. 180—183°/1 mm. αβ-*Di*-2-*hydroxy*-cis-*decahydro*-2-*naphthylacetylene* (similarly prepared), m.p. 125—126°, gives *di*-(? Δ^2)-cis-*octahydro*-2-*naphthylacetylene*, b.p. 215—220°/3 mm., whence H_2SO_4–AcOH at 5—8° gives a *substance*, (?) $C_{22}H_{32}O$, b.p. 215—222°/3 mm., dehydrogenated to a *substance*, m.p. 182—183° (not the expected 2 : 3 : 6 : 7-dibenzphenanthrene).

R. S. C.

Synthetic investigations on the degradation products of bile acids, sex hormones, etc. I. Synthesis of 7-methyldi*cyclo*-[0 : 3 : 3]-octan-1-one. II. Synthesis of ketodeoxycestric acid. D. K. Banerjee (*J. Indian Chem. Soc.*, 1940, **17**, 423—428, 453—462).—I. Distillation of $COMe{\cdot}[CH_2]_2{\cdot}CO_2Et$ and $CN{\cdot}CH_2{\cdot}CO_2Et$ with NH_2Ac and glacial AcOH (vapours at 105—110°) yields a residue of *Et* α-*cyano*-β-*methyl*-Δ^{α}-*butene*-αδ-*dicarboxylate*, b.p. 154—160°/5·5 mm., which with aq. KCN followed by cold aq. HCl yields *Et*$_2$ αβ-*dicyano*-β-*methyladipate*, b.p. 190—192°/6 mm., hydrolysed to *Et*$_3$ β-*methylbutane*-αβδ-*tricarboxylate*, b.p. 169—170°/10 mm., cyclised (Na in C_6H_6) to *Et*$_2$ 3-*methyl*cyclo*pentanone*-2 : 3-*dicarboxylate*, b.p. 153°/8·5 mm. The Na derivative of this with $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$ in C_6H_6 affords *Et*$_3$ 3-*methyl*cyclo*pentanone*-2 : 3-*dicarboxylate*-2-β-*propionate*, b.p. 194—197°/7 mm. [also obtained (poor yield) from the K derivative], hydrolysed to 3-*methyl*cyclo*pentanone*-3-*carboxylic*-2-β-*propionic acid*, m.p. 116° (*semicarbazone*, m.p. 228°), reduced (Clemmensen) and esterified to *Et*$_2$ 1-*methyl*cyclo*pentane*-1-*carboxylate*-2-β-*propionate*, b.p. 140—142°/4·5—5 mm. This is cyclised (Na in C_6H_6) to 30% of *Et* 7-*methyldi*cyclo-[0 : 3 : 3]-*octan*-1-*one*-2-*carboxylate*, b.p. 119—120°/6 mm., hydrolysed to 7-*methyldi*cyclo-[0 : 3 : 3]-*octan*-1-*one*, b.p. 70°/6 mm. (*semicarbazone*, m.p. 210°) (cf. Errington *et al.*, A., 1938, II, 269), oxidised (HNO_3) to 1-methylcyclopentane-1-carboxylic-2-acetic acid, m.p. 126—127° (mainly the *trans*-form).

II. $COMe{\cdot}[CH_2]_3{\cdot}CO_2Et$, $CN{\cdot}CH_2{\cdot}CO_2Et$, NH_2Ac, and glacial AcOH yield (as above) *Et* α-*cyano*-β-*methyl*-Δ^{α}-*pentene*-αε-*dicarboxylate*, b.p. 175—178°/7·5 mm., and thence *Et*$_2$ αβ-*dicyano*-β-*methylpimelate*, b.p. 192—193°/4 mm., hydrolysed and esterified to *Et*$_2$ β-*carbethoxy*-β-*methylpimelate*, b.p. 168°/6 mm. Cyclisation (Na in C_6H_6) of this yields a *compound*, $C_{13}H_{20}O_5$, b.p. 156°/7 mm. $CN{\cdot}CNaPh{\cdot}CO_2Et$ with $Cl{\cdot}[CH_2]_2{\cdot}COMe$ in C_6H_6 yields *Et* α-*cyano*-γ-*acetyl*-α-*phenylbutyrate*, b.p. 172—175°/5 mm. (*semicarbazone*, m.p. 154—155°), hydrolysed to γ-*acetyl*-α-*phenylbutyric acid*, b.p. 195—197°/6 mm., the *Et* ester, b.p. 143—145°/4·5 mm. (*semicarbazone*, m.p. 119—120°), of which with $CN{\cdot}CH_2{\cdot}CO_2Et$, NH_2Ac, and AcOH affords *Et* α-*cyano*-ε-*phenyl*-β-*methyl*-Δ^{α}-*pentene*-αε-*dicarboxylate*, b.p. 200—208°/4 mm. Addition of HCN and hydrolysis of the product converts this into δ-*carboxy*-α-*phenyl*-δ-*methylpimelic acid*, m.p. 169—171°, the *Et*$_4$ ester, b.p. 202—204°/5 mm., of which is cyclised (Na in C_6H_6) to *Et*$_2$ 6-*phenyl*-3-*methyl*cyclo*hexanone*-2 : 3-*dicarboxylate*, b.p. 195—197° (some decomp.)/5 mm. The Na derivative of this with $CH_2Br{\cdot}CO_2Et$ in C_6H_6 and the K derivative with $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$ in xylene yield (after hydrolysis and esterification) respectively *Et*$_2$ 6-*phenyl*-3-*methyl*cyclo*hexanone*-3-*carboxylate*-2-*acetate* (I), b.p. 180—186°/2·5 mm., and -β-*propionate*, b.p. 185—190°/1·6 mm. [together with *Et* 6-*phenyl*-3-*methyl*cyclo*hexanone*-3-*carboxylate*, b.p. 182—187°/6 mm. (*semicarbazone*, m.p. 175·5—176·5°) in each case]. (I) with Zn wool, $CH_2Br{\cdot}CO_2Et$, and a trace of I in PhMe affords *Et*$_3$ 2-*phenyl*-5-*methyl*-Δ^1-cyclo*hexene*-5-*carboxylate*-1 : 6-*diacetate*, b.p.



(II.)

186—200°/1·8 mm., which on prolonged boiling with excess of red P and HI (*d* 1·7) followed by treatment of the product with conc. H_2SO_4 at 100° (bath) yields ketodeoxyœstric acid (**II**) (*semicarbazone*, m.p. 165—175°). A. Li.

Synthesis of 6-hydroxy-17-equilenone (an isomeride of equilenin) and two of its homologues. W. E. Bachmann and D. W. Holmes (*J. Amer. Chem. Soc.*, 1940, **62**, 2750—2757; cf. A., 1939, II, 261; 1940, II, 225).—1-Keto-9-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene (modified prep. starting from 4 : 1-OMe·$C_{10}H_6$·CO·$[CH_2]_2$·CO_2H), m.p. 99—100° (lit. 98°), gives (methods : *loc. cit.*) *Me* 1-*keto*-9-*methoxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*glyoxylate*, m.p. 124—124·5°, *Me* 1-*keto*-9-*methoxy*- (**I**), m.p. 120·5—121°, and 1-*keto*-9-*methoxy*-2-*methyl*- (**II**), m.p. 137—137·5°, -1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*. Hydrolysis of (**II**) by KOH–aq. MeOH and then sublimation at 200°/0·4 mm. gives 1-*keto*-9-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 82—83°. With $CH_2Br·CO_2Me$ and Zn, (**II**) gives Me_2 1-*hydroxy*-9-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*-1-*acetate* (**III**), m.p. 130—131°, and thence anti-9-*methoxy*-2-*carboxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylideneacetic acid* (**IV**), m.p. 224·5—226° (decomp.; bath preheated at 215°), and the *anhydride*, m.p. 239—240·5°, sublimes at 220°/0·4 mm., of the *syn*-isomeride. Partial hydrolysis of the Me_2 ester, m.p. 104·5—105°, of (**IV**) gives the 2-Me_1 ester, m.p. 197·5—199° (decomp.), the K salt of which is oxidised by $KMnO_4$ to (**II**), thus proving survival of the C-skeleton. Treatment of (**III**) with, successively, $SOCl_2$–C_5H_5N–C_6H_6, boiling KOH–MeOH, 45% aq. KOH at 100°, and 2% Na–Hg in warm H_2O gives α- (~28%), m.p. 233—235° (bath preheated at 220°), and β-9-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylic*-1-*acetic acid* (~51%), m.p. 228·5—230° (decomp.), also obtained similarly from the K salts of the unsaturated acids or (1 part of α- and 6 parts of β-acid) by hydrogenating (PtO_2) (**IV**) in AcOH. CH_2N_2 then gives the α-, m.p. 107—108°, and β-Me_2 ester, m.p. 96—97°, which by partial hydrolysis give the 2-Me_1 esters, α-, m.p. 198·5—200°, and β-*form*, dimorphic, m.p. 190—192° and 202·5—204°, converted by the Arndt–Eistert process into *Me* β-9-*methoxy*-2-*carbomethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionate*, α-, m.p. 152·5—153·5°, sublimes at 200°/0·4 mm., and β-*form*, m.p. 75·5—76·5°. Cyclisation by NaOMe then gives *Me* 6-*methoxy*-17-*equilenone*-16-*carboxylate* (nomenclature : A., 1940, II, 349), α-, m.p. 151—152° (vac.), and β-*form*, m.p. 140—141° (vac.), which, when hydrolysed by HCl–AcOH–H_2O and then sublimed at 200°/0·01 mm., give 6-*methoxy*-17-*equilenone* (**V**), α-, m.p. 147·5—149° (vac.), and β-*form*, m.p. 112—113° (vac.), with small amounts of 6-*hydroxy*-17-*equilenone* (**VI**), α-, m.p. 240—242° (vac.; bath preheated at 220°), and β-*form*, m.p. (+ solvent) 101—102° (gas) and (solvent-free) 171·5—172·5° (vac.), also obtained from (**V**) by HCl–AcOH–H_2O–N_2. The Na derivative of (**I**) with EtBr gives *Me* 1-*keto*-9-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*, dimorphic, m.p. 95·5—97° and 113—114°, and thence (as above) Me_2 1-*hydroxy*-9-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*-1-*acetate*, m.p. 103·5—104·5°, anti-9-*methoxy*-2-*carboxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylideneacetic acid*, m.p. 203·5—205° (decomp.), and the *anhydride*, m.p. 228·5—229·5°, of the *syn*-acid, 9-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylic*-1-*acetic acid*, α-, m.p. 230·5—232·5°, and β-*form*, m.p. (+xC_6H_6) 155° (gas) and (solvent-free) 223—225° (Me_2 ester, α-, m.p. 133·5—134·5°, and β-*form*, m.p. 99·5—100·5°; 2-Me_1 ester, α-, m.p. 198·5—199·5°, and β-*form*, m.p. 160—161°), *Me* β-9-*methoxy*-2-*carbomethoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionate*, α-, m.p. 129—130°, and β-*form*, m.p. 73—74°, *Me* 6-*methoxy*-19-*methyl*-17-*equilenone*-16-*carboxylate*, α-, m.p. 161—162° (vac.), and β-*form*, 118—120° (vac.), 6-*methoxy*-, α-, m.p. 142—142·5°, and β-*form*, m.p. 75—76°, and 6-*hydroxy*-19-*methyl*-17-*equilenone* (**VII**), α-, m.p. 206—208° (vac.), and β-*form*, m.p. (+solvent) 109—110° (gas) and (solvent-free) 121·5—123°. By hydrolysis, the Arndt–Eistert and other reactions as above, β-9-*methoxy*-2-*carbomethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionic acid*, α-, m.p. 167·5—168·5°, and β-*form*, m.p. 135·5—137° (prep. from the Me_2 esters), gives *Me* γ-9-*methoxy*-2-*carbomethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthryl*-n-*butyrate*, α-, m.p. 94·5—95·5°, and β-form, an oil, "*Me* 6-*methoxy*-D-*homo*-17a-*equilenone*-17-*carboxylate*" [*Me* 3-*keto*-8-*methoxy*-2a-*methyl*-1 : 2 : 3 : 4 : 5 : 6 : 2*a* : 6*a*-*octahydrochrysene*-4-*carboxylate*], α-, m.p. 152—154° (vac.), and β-*form*, m.p. 150—151° (vac.), 6-*methoxy*-, α-, m.p. 131—132·5° (vac.), and β-*form*, m.p. 142—143°, and 6-*hydroxy*-D-*homo*-17a-*equilenone* (**VIII**), α-, m.p. 227—229° (vac.), and β-*form*, m.p. 223—225° (vac.). (**VI**) has no œstrogenic activity in 0·5-mg., (**VII**) and (**VIII**) have none in 1-mg., doses (both forms in all cases). R. S. C.

Ketonic bile acids.—See B., 1940, 898.

Constitution of pedicinin. P. K. Bose and P. Dutt (*J. Indian Chem. Soc.*, 1940, **17**, 499—507).—Pedicinin (**I**) (Na_2 salt), isolation (from *Didymorcarpus pedicellata*) described, is probably 2 : 5-*dihydroxy*-3-*methoxy*-6-*cinnamoyl*-1 : 4-*benzoquinone*; it is sol. in aq. $KHCO_3$. The constitution assigned by Sharma *et al.* (A., 1939, II, 274) is incorrect. (**I**) and Zn dust–Ac_2O at 100° (bath) afford *tetra-acetyldihydropedicinin* (2 : 3 : 5 : 6-*tetra-acetoxy*-4-*methoxyphenyl styryl ketone*), m.p. 207—208°, whilst (**I**) and H_2 (Pd–C; EtOH) at 30°/760 mm. afford a H_4-derivative (**II**) (probably 2 : 3 : 5 : 6-tetrahydroxy-4-methoxyphenyl β-phenylethyl ketone) (yellow), converted rapidly by air-oxidation into *dihydropedicinin* (2 : 5-*dihydroxy*-3-*methoxy*-6-β-*phenylpropionyl*-1 : 4-*benzoquinone*) (**III**), m.p. 134° (Na_2 salt), similarly reduced to (**II**). Similar hydrogenation of pedicellin (**IV**) affords dihydropedicellin, b.p. 135—145°/0·1 mm., converted by HNO_3 (*d* 1·4)–AcOH into a semi-solid product, hydrolysed by warm 5% aq. NaOH to (**III**). (**IV**) and HNO_3 (*d* 1·4)–AcOH (40—50 sec.) give mainly *methylpedicinin* (5-*hydroxy*-2 : 3-*dimethoxy*-6-*cinnamoyl*-1 : 4-*benzoquinone*); reaction for 1·5 min. affords much (**I**) also. A. T. P.

Extensions of the vitamin-K_1 synthesis. L. F. Fieser, M. Tishler, and N. L. Wendler (*J. Amer. Chem. Soc.*, 1940, **62**, 2861—2866).—Mainly a detailed account of work already reported (A., 1940, II, 226). The following appears new. The adduct of toluquinone and $(CH_2{:}CH)_2$ has m.p. 80—81°. 2-Methyl-5 : 8-dihydro-1 : 4-naphthaquinol has m.p. 173—174° (darkens at 170°). 2 : 3 : 5-Trimethyl-6-phytylquinol has m.p. 92°; the corresponding quinone with H_2–$PdCl_2$–MeOH, followed by Ag_2O–Et_2O, gives 2 : 3 : 5-*trimethyl*-6-*dihydrophytyl*-1 : 4-*benzoquinone*, an oil (*quinol diacetate*, m.p. 54—55°). α-Tocopherol allophanate has m.p. 175—176° (lit. 172°). R. S. C.

Hydro-, oxido-, and other derivatives of vitamin-K_1 and related compounds. M. Tishler, L. F. Fieser, and N. L. Wendler (*J. Amer. Chem. Soc.*, 1940, **62**, 2866—2871).—Partly a detailed account of work already reported (A., 1940, II, 226, 311; 1940, III, 820). Pt- or Pd-hydrogenation of vitamin-K_1 followed by oxidation (Ag_2O) of the resulting quinol gives always the H_6-compound, but partial hydrogenation in MeOH in presence of Raney Ni similarly affords the βγ-H_2-derivative. 2-*Dihydrophytyl*-1 : 4-*naphthaquinone*, an oil, is similarly obtained, but 3-γ-*phenyl*-n-*propyl*-2-*methyl*-1 : 4-*naphthaquinone*, m.p. 42°, is obtained by oxidation of the quinol from the $CHPh{:}CH·CH_2$ compound and H_2–$PdCl_2$ in MeOH. 2-Methyl-1 : 4-naphthaquinone and H_2–$PdCl_2$ in AcOH give 2-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 4-*naphthaquinol*, m.p. 165—167° (diacetate, m.p. 100—101°). Commercial 1 : 6-$C_{10}H_6Me_2$ is a mixture and affords 2 : 8- (**I**), m.p. 135—135·5°, and 2 : 5-*dimethyl*-1 : 4-*naphthaquinone* (**II**), m.p. 93·5—94·5°. Toluquinone and piperylene in dioxan at 60—70° give 1 : 4-*diketo*-2 : 8-*dimethyl*-5 : 8 : 9 : 10-*tetrahydronaphthalene* (**III**), softens at ~96°, m.p. (final) 101·5°, isomerised by $SnCl_2$–HCl–EtOH to 2 : 8-*dimethyl*-5 : 8-*dihydro*-1 : 4-*naphthaquinol*, m.p. 91—91·5°, which with CrO_3–AcOH–H_2O at 60° gives (**I**). The oily product formed with (**III**) affords (**II**) by a similar series of reactions. 4 : 1-, m.p. 83·5—84·5°, and 3 : 2-$C_{10}H_6Me·OH$, m.p. 160·9—161·5° (corr.), and 9-methylperinaphthen-7-one, m.p. 156·5—157·2° (corr.), are prepared by known methods. 1-Keto-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 140°/13 mm. (*semicarbazone*, m.p. 195—196°), best obtained from $CH_2Ph·CHMe·CH_2·CO_2H$ by 80% H_2SO_4 at 100°, with Se at 310—330° (25%) or S at 250° (30%) gives 3 : 1-$C_{10}H_6Me·OH$, m.p. 91—93·5°, solidifies, remelts at 93·5—94° (*benzoate*, m.p. 75—76°). 1-Keto-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, b.p. 136—137°/16 mm. (oxime, m.p. 98—99°; *semicarbazone*, m.p. 205—206°), with Br gives 41% of 2 : 1-$C_{10}H_6Me·OH$, m.p. 63—64° (*benzoate*, m.p. 94—95°; *acetate*, m.p. 81—82°), also obtained in 55% yield from 2 : 1-$C_{10}H_6Me·NH_2$. R. S. C.

Constitution of celastrol. III. O. Gisvold (*J. Amer. Pharm. Assoc.*, 1940, **29**, 432—434; cf. A., 1940, II, 138).—Celastrol (**I**) is probably a mono- or 3 : 4(or 2 : 3)-di-alkyl-8-hydroxy-

1 : 2(or -1 : 4)-naphthaquinone (total alkyl = $C_{12}H_{26}$), and has no significant antihæmorrhagic activity. Oxidation (aq. alkaline $KMnO_4$) of (I) gives a little ? 3 : 1 : 2-$OH{\cdot}C_6H_3(CO_2H)_2$, m.p. 242—244° (lit. 161—163°, 244°). Cryst. substances could not be obtained from (I) or methylcelastrol (II) by AcOH–CrO_3. Reductive acetylation of (II) affords the corresponding *quinol diacetate*, m.p. 210°.

F. O. H.

III.—TERPENES.

Cyanocamphoranilic acids and their rotatory powers. M. Singh and A. Singh (*J. Indian Chem. Soc.*, 1940, **17**, 485—486).—Camphoric anhydride and *p*- or *m*-$CN{\cdot}C_6H_4{\cdot}NH_2$ with a little fused NaOAc at 120—130° (bath) afford 4'-, m.p. 140°, $[\alpha]_D$ +58·0° in MeOH, +51·5° in EtOH, or 3'-*cyanocamphoranilic acid*, m.p. 108—110°, $[\alpha]_D$ +48·7° in MeOH, +38·8° in EtOH, respectively. Vals. of $[\alpha]$ are anomalous, resembling those for the Cl-derivatives (cf. A., 1928, 1377). A. T. P.

Enol-acetate in the triterpene series. E. R. H. Jones and K. J. Verrill (*J.C.S.*, 1940, 1512).—β-Amyranonyl acetate with KOAc and Ac_2O gives an *enol-acetate*, m.p. 225—227°, $[\alpha]_D^{20}$ +44° in $CHCl_3$. F. R. S.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Sapogenins. X. Carbon skeleton and the position of the second hydroxyl group of quillaic acid. P. Bilham and G. A. R. Kon (*J.C.S.*, 1940, 1469—1474).—Quillaic acid (I) with Na–EtOH and N_2H_4 in a sealed tube at 200° gives deoxyquillaic acid (II) and with $CH_2Ph{\cdot}OH$ instead of EtOH, *quillaol*, $C_{29}H_{46}O_3$, m.p. 147—150°, is obtained. Oxidation of Me deoxyquillaate to the diketo-ester followed by reduction gives *Me* 16-*keto-oleanolate*, m.p. 204—205°, which is hydrolysed (KOH) to a mixture of 16-*keto*-$\Delta^{12:13(?)}$-*oleanene* (III), m.p. 220—222°, $[\alpha]_D$ −146·9° in $CHCl_3$, and an isomeric *ketone*, m.p. 160—161°, $[\alpha]_D$ +13° in $CHCl_3$. Reduction of (III) with Na–EtOH yields 16-*hydroxy*-$\Delta^{12:13(?)}$-*oleanene*, m.p. 179°, surface-film measurements of which show that the second OH of (I), $OH^{(2)}$, is situated on $C_{(16)}$ in ring D and it can be inferred that the CO_2H must be attached to $C_{(17)}$ at the junction of rings D and E. Reduction (Na–EtOH) of (II) and of (III) gives a *hydrocarbon*, $C_{29}H_{48}$, m.p. 193—193·5°, $[\alpha]_D$ +23° in $CHCl_3$, which is evidently a stereoisomeride of Winterstein and Stein's oleanene II (A., 1932, 856), from which it differs by the *trans*-locking of rings D and E. This has been converted into oleanene III (cf. Winterstein *et al.*, A., 1933, 718), proving that the C skeleton of (I) must be identical with that of oleanolic acid and gypsogenin. F. R. S.

Sarcostin. I. Preliminary study of its behaviour with reagents. J. W. Cornforth and J. C. Earl (*J.C.S.*, 1940, 1443—1447).—Sarcostin (I) with cold conc. HCl gives an amorphous product, $C_{21}H_{28}O_3$. Oxidation of (I) with $Pb(OAc)_4$ results in the use of 3—4 mol. proportions, the first very rapidly, with the formation of MeCHO, a neutral *product*, $C_{21}H_{32}O_6$, m.p. 186—187°, succinic acid, 2-*methyl*-1 : 3-cyclo*pentanedione* (II) (?), $C_6H_8O_2$, m.p. 210°, and non-cryst. material. The $(OAc)_3$-derivative of (I) with $Pb(OAc)_4$ yields a ketonic *substance*, $C_{27}H_{40}O_{10}$, m.p. 90—110°, solidifying and m.p. 164—165° [*semicarbazone*, m.p. 150—170° (decomp.)], which is oxidised ($KMnO_4$) to a *substance*, $C_{23}H_{36}O_6$ or $C_{19}H_{30}O_5$, m.p. 161—162°. Hydrogenation of (I) with PtO_2–H_2 affords *dihydrosarcostin*, $C_{21}H_{36}O_6$, m.p. 245—246°, oxidised [$Pb(OAc)_4$; 2 mols.] to MeCHO, a neutral *product*, $C_{19}H_{28}O_5$, m.p. 194—195°, and (II); the H_2-compound forms a $(OAc)_3$-derivative, m.p. 246—247°. Dehydrogenation of (I) with Se appears to give Diels' hydrocarbon and condensation with $COMe_2$ affords a *product*, m.p. 225—226°, containing 1 mol. of (I) to 2 mols. of $COMe_2$. (I) must contain a double bond, a $CHMe{\cdot}OH$ side-chain, and two glycol groups.

F. R. S.

Constituents of the higher fungi. II. Unsaturated system of polyporenic acid *A*. L. C. Cross and E. R. H. Jones (*J.C.S.*, 1940, 1491—1493).—Hydrogenation (H_2–PtO_2) of polyporenic acid *A* (I) gives the *H*$_2$-*acid* A, m.p. 216°, $[\alpha]_D^{20}$ +66° in C_5H_5N, which forms a *Me* ester, m.p. 142°, $[\alpha]_D^{20}$ +76° in $CHCl_3$, and *Me ester-acetate* (II), m.p. 142°, $[\alpha]_D^{20}$ +36° in $CHCl_3$. Ozonolysis of the Me ester-acetate of (I) yields a 50% amount of CH_2O and a small quantity of *Me ester keto-acetate* (?), m.p. 194°, $[\alpha]_D^{20}$ +121° in $CHCl_3$, whilst (II) similarly affords < 4% of CH_2O, indicating that the reactive double bond of (I) must be present in an exocyclic CH_2 group. The Me ester of (I) with HCO_2H gives the *Me ester-formate* (+0·5MeOH), m.p. 148°, $[\alpha]_D^{20}$ +84° in $CHCl_3$, and it is not cyclised.

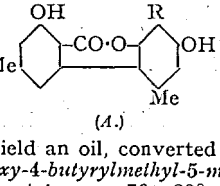
F. R. S.

Chemical investigation of Indian fruits. I. Bitter principles of pamparapanas (Indian shaddock). T. R. Seshadri and J. Veeraraghaviah (*Proc. Indian Acad. Sci.*, 1940, **11**, A, 505—511).—Methods are described for isolating the bitter principles of the peels (best dried), rags, and seeds of this plant. The first two contain 0·13% and 1% of naringin (I), respectively, whilst the seeds contain 0·15% of (I), ~0·6% of limonin (II), with ~0·03% of *iso*limonin (III). (I) has not been observed before in citrus seeds. The properties of (III) observed by Higby (A., 1939, III, 343) (contrary to those previously described) are confirmed. Attempted methylation of (II) is unsuccessful. Shaddock peels have advantages as cattle fodder. E. W. W.

Soil and peat humic acids. I. Isolation and purification of the acids. G. C. Esh and S. S. Guha-Sircar (*J. Indian Chem. Soc.*, 1940, **17**, 326—331).—Fats, waxes, and resinous matters are removed from the soil by extraction with C_6H_6–EtOH (1 : 1) and the residue is treated with 2% HCl at 100° for 1·5 hr. After treatment with H_2O at 100° the product is stirred with cold 4% KOH in a closed vessel for 8—10 hr. After three such treatments, the dark humate solutions are acidified with dil. HCl and the pptd. humic acid is thoroughly washed with H_2O. After repetition of the alkali–acid treatment, the dried material is separated into EtOH-sol. hymatomelanic acid (I) and EtOH-insol. humic acid (II); the latter is extracted with AcBr, washed with Et_2O, and dried at 80—85°. The ash in peat humic acids is greyish-white in colour and contains Fe, Si, Al, Mg, and traces of Cu whereas that of (II) is reddish-brown showing is high % of Fe. (I) has a relatively low ash content. OMe is not high in any humic acid and Ac is absent. The acids do not evolve appreciable amounts of furfuraldehyde when boiled with 12% HCl. CH_2O_2 appears to be absent. H. W.

V.—HETEROCYCLIC.

Kostanecki–Robinson reaction. II. Propionylation and butyrylation of orcacetophenone and its monomethyl ether. S. M. Sethna and R. C. Shah (*J. Indian Chem. Soc.*, 1940, **17**, 487—494; cf. A., 1940, II, 285).—Orcacetophenone (I) and $EtCO_2Na$–$(EtCO)_2O$ at 180—190° afford an oil, converted by conc. H_2SO_4 at room temp. into 7-*hydroxy*-4-*propionylmethyl*-3 : 5-*dimethylcoumarin*, m.p. 207—209° [*acetate*, m.p. 111—113°; *Me ether* (II), m.p. 75—77°; 2 : 4-*dinitrophenylhydrazone*, m.p. 255—256° (decomp.)], which with 60% aq. NaOH at room temp. gives 7-*hydroxy*-3 : 4 : 5-*trimethylcoumarin*, m.p. 195—197° (*Me ether*, m.p. 90—92°). Orcacetophenone 4-Me ether (III), as above, affords (II), whilst the Me_2 ether (IV) and $EtCO_2Et$–Na, with cooling, and then at 115—120°, give 2' : 4'-*dimethoxy*-6'-*methylbenzoylpropionylmethane*, b.p. 185—190°/2—4 mm., converted by HBr (*d* 1·78) into 7-*methoxy*-5-*methyl*-2-*ethylchromone*, m.p. 130—132°, demethylated by HI (*d* 1·7)–Ac_2O at 130—140° to the 7-*OH*-compound, m.p. 195—197°. *p*-Orsellinic acid (V), $CHAcMe{\cdot}CO_2Et$, and conc. H_2SO_4 at 60—70° for 16 hr. [4 hr. gives (V) only] give a small amount of a *substance*, m.p. 235—237° (decomp.) [probably (*A*), R = CO_2H], obtained similarly from (V)–H_2SO_4; at 240—250° it affords a *substance*, m.p. 265—267° [probably (*A*), R = H]. (I) and Pr^aCO_2Na–$(Pr^aCO)_2O$ at 180—190° yield an oil, converted by H_2SO_4 at room temp. into 7-*hydroxy*-4-*butyrylmethyl*-5-*methyl*-3-*ethylcoumarin*, m.p. 155—156° [*acetate*, m.p. 79—80°; *Me ether*, m.p. 51—54°; 2 : 4-*dinitrophenylhydrazone*, m.p. 253—254° (decomp.)], and thence by 10% aq. NaOH at room temp. into 7-*hydroxy*-4 : 5-*dimethyl*-3-*ethylcoumarin*, m.p. 170—172° (*Me ether*, m.p. 79—81°). (III) and Pr^aCO_2Na–$(Pr^aCO)_2O$ at 180—190° give an impure oil, but (IV) similarly, at 115—120°, affords 2 : 4-*dimethoxy*-6-*methylbenzoylbutyrylmethane*, b.p. 220—225°/20—25 mm. (*Cu* salt, m.p. 175—177°), converted by HBr (*d* 1·78) into 7-*methoxy*-, m.p. 97—98°, and thence [HI (*d* 1·7)–Ac_2O at 145—155°] -*hydroxy*-5-*methyl*-2-n-*propylchromone*, m.p. 163—165°.



(*A*.)

A. T. P.

Chromones of the naphthalene series. III. Rapid quantitative transformation at room temperature of *o*-aroyloxyacetoarones into *o*-hydroxydiaroylmethanes. V. V. Ullal, R. C. Shah, and T. S. Wheeler (*J.C.S.*, 1940, 1499—1500).—NaOEt–EtOH is an effective reagent for the rapid quant. transformation at room temp. of *o*-aroyloxyacetoarones into the corresponding *o*-hydroxydiaroylmethanes, which can be readily cyclised at room temp. to the corresponding chromones. The following are described: 2-p-*anisoyloxy*-, m.p. 122°, 2-(1′-*naphthoyloxy*)-, m.p. 113°, 2-(2′-*naphthoyloxy*)-, m.p. 103°, 2-(3′-*methoxy*-2′-*naphthoyloxy*)-, m.p. 116°, 2-(1′-*methoxy*-2′-*naphthoyloxy*)-, m.p. 122°, and 2-*palmityloxy*-1-*acetonaphthone*, m.p. 40°, and 2-*cinnamoyloxy*-4-*methoxyacetophenone*, m.p. 99°; *benzoyl*-2-*hydroxy*-, m.p. 137°, p-*anisoyl*-2-*hydroxy*-, m.p. 102°, and 2-*hydroxydi*-1-*naphthoyl*-, m.p. 163°; 2-*hydroxy*-, m.p. 136°, 2-*hydroxy*-3′-*methoxy*-, m.p. 175°, and 2-*hydroxy*-1′-*methoxy*-1 : 2′-*dinaphthoyl*-*methane*, m.p. 165°; 2-*hydroxy*-1-*naphthoylpalmitylmethane*, m.p. 112°; and 2-*hydroxy*-4-*methoxybenzoylcinnamoylmethane*, m.p. 140°; 2-(1′-*naphthyl*)-, m.p. 159°, 2-(2′-*naphthyl*)-, m.p. 198°, 2-(3′-*methoxy*-2′-*naphthyl*)-, m.p. 168°, 2-(1′-*methoxy*-2′-*naphthyl*)-, m.p. 144°, 2-*pentadecyl*-, m.p. 89°, 2-(3′-*hydroxy*-2′-*naphthyl*)-, m.p. >300° (*acetate*, m.p. 153°), and 2-(1′-*hydroxy*-2′-*naphthyl*)-5 : 6-*benzochromone*, m.p. >300° (*acetate*, m.p. 189°).

F. R. S.

***N*-Vinylethinylmethylpiperidine.**—See B., 1940, 780.

Cyanine dyes of the pyridine series. M. Q. Doja (*J. Indian Chem. Soc.*, 1940, **17**, 347—350).—2-p-*Dimethylaminostyrylpyridine methochloride*, m.p. 117°, *methobromide*, m.p. 262°, and methiodide and the p-*dimethylaminoanils* of 2-*methylpyridine methochloride* and *methobromide*, m.p. 235° and 237°, respectively, have been prepared. The absorption spectra and fluorescence of these substances are described. H. W.

α-Pyridinium compounds of higher fatty acids and amides.—See B., 1940, 778.

Tetrahydroisoquinolino-alcohols derived from tetrahydronaphthalene. E. Mosettig and E. L. May (*J. Org. Chem.*, 1940, **5**, 528—543).—1-*Keto*-6-*acetoxy*-, m.p. 61—62°, 1-*keto*-7-*hydroxy*-, m.p. 162—164°, and 1-*keto*-7-*acetoxy*-, m.p. 79—80°, -1 : 2 : 3 : 4-*tetrahydronaphthalene* are described. 2-*Bromo*-1-*keto*-7-*methoxy*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 78—80°, could not be caused to react with tetrahydroisoquinoline or piperidine. 1-Keto-1 : 2 : 3 : 4-tetrahydronaphthalene, CH_2O, and tetrahydroisoquinoline hydrochloride at 100° afford 1-*keto*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 90—91° (*picrate*, m.p. 118—120° after softening at 86°). Attempts to hydrogenate the ketone (PtO_2 in EtOH) lead to fission into base and 1-keto-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, whereas the hydrochloride is hydrogenated to 1-*hydroxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 94·5—95° [*hydrochloride*, m.p. 202—203° (decomp.)]. 1-*Keto*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 95°, gives a *hydrochloride*, m.p. 219—221° (decomp.) after softening at 146°, which is reduced to the 1-*hydroxy*-base, m.p. 95·5—96° (*hydrochloride*, m.p. 182·5—184°). 1-*Keto*-6-*methoxy*-2-1′ : 2′ : 3′ : 4-*tetrahydro*-2-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 146—147°, is reduced to the 1-*OH*-base, m.p. 125·5—126° (corr.) [*hydrochloride*, m.p. 178—179° (decomp.)]. The non-cryst. 1-*keto*-6-*methoxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene* gives a *hydrochloride*, m.p. 127—128° and 218° (decomp.) after evolution of gas and resolidification at 160°. This is hydrogenated (PtO_2 in 95% EtOH) to the 1-*OH*-base, m.p. 124·5—125° (corr.), which is converted by HCl–EtOH or Ac_2O–C_5H_5N into (?) 6-*methoxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-3 : 4-*dihydronaphthalene*, m.p. 135·5—136°; the *hydrochloride*, m.p. 201—202·5°, appears to be reduced (H–PtO_2–EtOH) to 6-methoxytetrahydroisoquinoline and 6-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene. 1-*Keto*-6-*acetoxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 151—152°, is hydrolysed to the 1-*OH*-base, m.p. 156—157° (decomp.) [*hydrochloride*, m.p. 158—160° (decomp.)], and reduced (PtO_2 in 95% EtOH) to 1-*hydroxy*-6-*acetoxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride* (I), m.p. 189—192·5° (decomp.). Reduction of the appropriate ketone leads to 1 : 6-*dihydroxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. (indef.) 111—121° (decomp.) [*hydrochloride*, m.p. 105—107° (decomp.) and 190—196° (decomp.) after resolidification]. Hydrolysis (KOH–MeOH) of (I) yields 6-*hydroxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-3 : 4-*dihydronaphthalene*, m.p. 136—137° (corr.) [*hydrochloride*, m.p. 187—188° (decomp.) or, +MeOH, m.p. 126—128·5° (decomp.); *hydrochloride* of Ac derivative, m.p. 204—206·5° (decomp.)], hydrogenated to tetrahydroisoquinoline and 6-*hydroxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 88—88·5° (corr.). 1-*Keto*-6-*aceloxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 200—202° (decomp.) after softening at 162°, is reduced to the 1-*OH*-compound (*hydrochloride*, m.p. 181·5—183°) and hydrolysed to the 1 : 6-(*OH*)$_2$-base, m.p. 145·5—146·5° (corr.) [*hydrochloride*, m.p. 207—208°, acetylated to a *substance*, $C_{23}H_{26}O_3NCl$, m.p. 203—204·5° (decomp.)]. 1-*Keto*-7-*methoxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 104—105° (corr.) [*hydrochloride*, m.p. 119—120° (corr.)], is formed with a *by-product*, $C_{24}H_{24}O_4$, m.p. 138—139° (corr.), by the customary method. It is reduced to the 1-*OH*-compound, m.p. 111·5—112° (corr.) [*hydrochloride*, m.p. 207·5—209° (decomp.); *Ac* derivative *hydrochloride*, m.p. 167·5—169·5°]. 1-*Keto*-7-*methoxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 220—221° (decomp.) after softening at 156°, is reduced to the 1-*OH*-base, m.p. 135—135·5° (corr.) [amorphous *hydrochloride*, m.p. 154—163°; *picrate*, m.p. 150—151·5°; *Ac* derivative *hydrochloride*, m.p. 182·5—183·5°]. 1-*Keto*-7-*acetoxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m.p. 209—211° (decomp.) after softening at 158°, gives the 1-*OH*-compound (*hydrochloride*, m.p. 149—160°). 1 : 7-*Dihydroxy*-2-6′-*methoxy*-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 173—174·5° (corr.), gives a *hydrochloride*, m.p. 209°. 1-*Hydroxy*-2-1′ : 2′ : 3′ : 4′-*tetrahydro*-2′-isoquinolylmethyl-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 133·5—134° (corr.), did not yield a cryst. hydrochloride or picrate.

H. W.

Sulphonamides. I. G. L. Juneja, K. S. Narang, and J. N. Ray (*J. Indian Chem. Soc.*, 1940, **17**, 495—498).—*p*-NHAc·C_6H_4·SO_2Cl and the respective aminoquinoline in dry $CHCl_3$ give 5-, m.p. 254° (decomp.), 6-, m.p. 283°, or 8-*p*-acetamido-, m.p. 194°, and thence [HCl (*d* 1·15) at 100° (bath)] 5-, m.p. 226—228°, 6-, m.p. 200°, or 8-*p*-amino-benzenesulphonamidoquinoline, m.p. 188° (cf. Bobrański, A., 1939, II, 179). 6-Aminoquinoline and CH_2Cl·COCl in dioxan at 70° (2 min.) afford 6-p-*chloro*-, m.p. 166—168° (decomp.), converted by $NHEt_2$ or piperidine in EtOH into 6-p-*diethylamino*-, m.p. 137°, or 6-p-*piperidino*-*acetamidobenzenesulphonamidoquinoline*, m.p. 131°, respectively. Similarly prepared are: 6-p-*chloro*- (*hydrochloride*), -*diethylamino*-, m.p. 147—149°, and -*piperidino*-*propionamido*-, m.p. 198—201°; 8-p-*chloro*- [*hydrochloride*, m.p. 220° (decomp.)], -*diethylamino*-, m.p. 115—116°, and -*piperidino*-*acetamido*-, m.p. 172—173°; 8-p-*chloro*- [*hydrochloride*, m.p. 228° (decomp.)], -*diethylamino*-, m.p. 95—96°, and -*piperidino*-*propionamido*-, m.p. 178°; 5-p-*chloro*- (*hydrochloride*, m.p. 226°) and -*piperidino*-*acetamidobenzenesulphonamidoquinoline*, m.p. 217—218°. Encouraging results are reported when some of the above compounds are tested on mice infected with pneumococci. A. T. P.

Phthalocyanines.—See B., 1940, 784.

Chemotherapy of malaria. 6-Methoxyquinolyl-8-hydrazine and synthesis of some heterocyclic compounds from it. B. K. Nandi (*J. Indian Chem. Soc.*, 1940, **17**, 449—452).—6-*Methoxyquinolyl*-8-*hydrazine* (I), m.p. 67° (from 6-methoxy-8-aminoquinoline, HNO_2, and $SnCl_2$), with dil. HCl and KCNS yields 1-(6′-*methoxyquinolyl*-8′)-*thiosemicarbazide*, m.p. 259—261°, which with COPh·CH_2Br in boiling EtOH gives 2-(8′-*hydrazino*-6′-*methoxyquinolyl*)-4-*phenylthiazole*, m.p. 121—124°. *cyclo*Hexanone in EtOH with (I) in dil. AcOH gives the 6-*methoxyquinolyl*-8-*hydrazone*, m.p. 91°, converted by warm dil. H_2SO_4 into the sulphate of 6′-*methoxyquinolino*-(7′ : 8′ : 3 : 2)-4 : 5 : 6 : 7-*tetrahydroindole*, m.p. 181—182° (*hydrochloride*, m.p. 256—259°). With CH_2Ac·CO_2Et at 100° (I) yields a product, m.p. 72°, which when heated gives 1-(6′-*methoxyquinolyl*-8′-)3-*methylpyrazol*-5-*one*, m.p. 135°. The hydrochloride of (I) with $AcCO_2H$ yields a product converted by boiling conc. HCl into 6′-*methoxyquinolino*-(7′ : 8′ : 3 : 2)-*pyrrole*-5-*carboxylic acid*, m.p. 197—198°. With

KCNO (I) yields 1-(6'-*methoxyquinolyl*-8')-*semicarbazide*, m.p. 236—239° (softening at 225°), and with *dl*-arabinose in dil. AcOH, the 6-*methoxyquinolyl*-8-*hydrazone*, m.p. 140°. A. Li.

Chemotherapy of bacterial infections. III. Synthesis of (N^4)-amino-substituted heterocyclic derivatives of sulphanilamide. K. Ganapathi (*Proc. Indian Acad. Sci.*, 1940, **12, A**, 274—283).—*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, HCl, and KCNS give p-*sulphonamidophenylthiocarbamide* (I), m. p. 197°, converted by $CH_2Cl{\cdot}CHCl{\cdot}OEt$ in boiling H_2O into 2-p-*sulphonamidoanilinothiazole* or 2-p-*sulphonamidoanilothiazoline*, m.p. 240° (decomp.). Similar reactions lead to 2-p-*sulphonamidoanilo*-3-*allyl*-, m.p. 139·5—141°, and -3-*phenyl*-, m.p. 193°, -*thiazoline*. 2-p-*Sulphonamidoanilo*-4-*phenyl*-3-*allylthiazoline*, m.p. 209—210°, and 2-p-*sulphonamidoanilino*-4-*phenylthiazole* (or 2-p-*sulphonamidoanilo*-4-*phenylthiazoline*), m.p. 228—230°, are described. Condensation of (I) with $CHAcBr{\cdot}CO_2Et$ or $CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ in H_2O at 100° yields *Et* 2-p-*sulphonamidoanilino*-4-*methylthiazole*-5-*carboxylate*, m.p. 243—245°, and *Et* 2-p-*sulphonamidoanilinothiazolyl*-4-*acetate* (or *Et* 2-p-*sulphonamidoanilothiazolinyl*-4-*acetate*), m.p. 219—220° (slight decomp.). $CHAcBr{\cdot}CH_2{\cdot}CO_2Et$ similarly gives *Et* 2-p-*sulphonamidoanilino*-4-*methylthiazolyl*-5-*acetate* (or *Et* 2-p-*sulphonamidoanilo*-4-*methylthiazolinyl*-5-*acetate*), m.p. 163° after softening at 154°. (I) and $CH_2Cl{\cdot}CO_2Et$ or $CH_2Cl{\cdot}CO_2H$ in boiling abs. EtOH or $CH_2Cl{\cdot}COCl$ in $COMe_2$ afford N-p-*sulphonamidophenyl*-ψ-*thiohydantoin*, m.p. (indef.) 240—255°, accompanied by $NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ if reaction is prolonged or effected in dil. EtOH or H_2O. N^1-*p*-Sulphonamidophenyl-*N*-allylthiocarbamide and I in boiling EtOH followed by NH_3 give 2-p-*sulphonanilino*-5-*iodomethylthiazoline* (or 2-p-*sulphonamidoanilo*-5-*iodomethylthiazolidone*), m.p. 115—119°. Diazotisation of 2-N'-sulphanilamidothiazole and coupling with 4-aminothiouracil leads to 4-*amino*-5-[4'-(2)-*thiazolylsulphonamidophenylazo*]*thiouracil*. 2-(4-N'-*Sulphanilamidobenzenesulphonamido*)*thiouracil* has m.p. 163—168°. 5-Chloroacridine (improved prep. described) is dissolved in 5—8 times its wt. of PhOH at 100° and the solution is heated with the powdered amine, $NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NHR$, thereby giving N^4-5-*acridylsulphanilamide*, m.p. 245—246°, 2-N^4-5-*acridylsulphanilamidopyridine*, m.p. 268—269° (decomp.), and 4-N^4-5-*acridylsulphanilamido*-*aniline*, m.p. 278—282°, -*nitrobenzene*, m.p. >285°, and -*benzenesulphonamide*, m.p. >280°. None of the thiazole and related derivatives shows any activity in streptococcal or pneumococcal infections in mice. Some of the acridine compounds exhibit considerable activity in streptococcal infections; they are inactive in pneumococcal infections. For pronounced antibacterial action the heterocyclic ring should be substituted in the sulphonamide radical leaving a free NH_2-group which appears to play some significant but imperfectly understood rôle in the mechanism of therapeutic action. H. W.

Cyanine dyes.—See B., 1940, 846, 847.

Alkaloid of *Berberis umbellata*, Wall. I. Isolation and examination of umbellatine. R. Chatterjee (*J. Indian Chem. Soc.*, 1940, **17**, 289—291).—The stem bark yields optically inactive *umbellatine* (I), $C_{21}H_{21}O_8N$, m.p. 206—207° (decomp.), which when crystallised from H_2O contains $5{\cdot}5H_2O$; $0{\cdot}5H_2O$ is retained at 110°/vac. whilst at 120° slight decomp. commences. (I) contains 2 OMe and appears to be a *sec.* amine since it gives a cryst. *methiodide* and *nitrosoumbellatine*, m.p. 265—267° (decomp.). The presence of 1 CH_2O_2 group is confirmed. *Umbellatine hydrochloride* and *platinichloride*, which char without melting, are described. H. W.

Synthesis of benzonicotine. B. K. Nandi (*J. Indian Chem. Soc.*, 1940, **17**, 285—288).—Addition of Et quinoline-3-carboxylate and 1-methylpyrrolid-2-one to EtOH-free NaOEt in C_6H_6 gives 3'-1'-*methylpyrrolid*-2'-*onyl* 3-*quinolyl ketone*, m.p. 120° (*monopicrate*, m.p. 178°), converted by fuming HCl at 140—145° into 3-*quinolyl* γ-*methylamino*-n-*propyl ketone*, b.p. 165—175°/0·01 mm. (*platinichloride*, m.p. 215—220°). This is reduced (H_2–Pd–C–"extra norite" in HCl–EtOH) to 3-*quinolyl*-γ-*methylamino*-n-*propylcarbinol*, b.p. 200—204°/0·5 mm. (*platinichloride*, m.p. 286—288°; *dipicrate*, m.p. 199—201°), in poor yield, which with HI (*d* 1·94) and red P at 100—110° affords α-3-quinolyl-δ-methylamino-*n*-butyl iodide, converted into r-*benzonicotine* (I), b.p. 172—175°/0·1 mm. [*dipicrate*, m.p. 224—225°; *platinichloride*, m.p. 232—234°; *aurichloride*, m.p. 239—240° (decomp.)]. Physiologically natural *l*-nicotine is three times as active as (I). H. W.

Alkaloids of fumariaceous plants. XXVIII. *Corydalis nobilis*, **Pers.** R. H. F. Manske (*Canad. J. Res.*, 1940, **B, 18**, 288—292).—This plant contains protopine, cryptopine, *d*- and *dl*-tetrahydropalmatine, stylopine, *d*-*iso*corypalmine (I), corytuberine (II), biculline (III), and corlumine, with three unidentified bases, one non-phenolic, *alkaloid F* 53, $C_{17}H_{17}O_4N$ (?), m.p. 183°, and two phenolic, *alkaloid F* 54, $C_{17}H_{19}O_3N(OMe)_2$, m.p. 143°, and *alkaloid F* 55, m.p. 209°. Taxonomically, the plant is unique in forming both (II) and (III); its roots do not contain acctylornithine. Alkaloid F 34, m.p. 218°, from *C. caseana* (A., 1938, II, 383) is identical with the *dl*-form of (I). E. W. W.

VI.—ORGANO-METALLIC COMPOUNDS.

Alkyl esters of mono- and di-arylarsenious acids. G. Kamai and V. M. Zoroastrova (*J. Gen. Chem. Russ.*, 1940, **10**, 921—926).—The following esters were prepared by the reaction $AsPhCl_2 + NaOR \rightarrow AsPh(OR)_2$: R = Me, Et, *Pr*$^{\alpha}$, b.p. 128—129°/8 mm., *Pr*$^{\beta}$, b.p. 118—119°/11 mm., *Bu*$^{\alpha}$, b.p. 147—148°/10 mm., *Bu*$^{\beta}$, b.p. 144—144·5°/12 mm., *iso*amyl, b.p. 153—154·5°/11 mm. The esters AsRR'·OR'' were obtained analogously: R = R' = Ph, R'' = Et [*compound*, m.p. 160—162° (decomp.), with CuI], R'' = *Pr*$^{\alpha}$, b.p. 174—175°/10 mm. (*compound*, m.p. 140—142°, with CuI); R = Ph, R' = *p*-C_6H_4Me, R'' = *Pr*$^{\alpha}$, b.p. 188—189°/11 mm. Isomerisation of these esters does not occur when they are heated with alkyl halides. R. T.

VIII.—ANALYSIS.

Manometric carbon determination. D. D. Van Slyke and J. Folch (*J. Biol. Chem.*, 1940, **136**, 509—541).—A combustion mixture of furming H_2SO_4, H_3PO_4, CrO_3, and HIO_3 effects complete oxidation in 1—3 min., giving theoretical yields of CO_2 with compounds hitherto resistant to wet combustion (cholesterol, palmitic acid, etc. The CO_2 is collected and measured in the Van Slyke–Neill manometric apparatus, a solution of NaOH and N_2H_4 being used for absorption (cf. A., 1933, 1314). Factors for calculation are derived. No modifications are required for substances containing N, S, halogen, or alkali metal. A. Li.

Calorimetric determination of small amounts of acetylene. T. F. Tschernakovskaja (*Sintet. Kautschuk*, 1936, No. 2, 29—31).—A measured vol. of C_2H_2 in $(CH_2{:}CH)_2$ and N_2 is passed through ammoniacal Cu solution containing gelatin (three preps. described) (Ilosvay–Schultze reagent; cf. A., 1916, ii, 649) and the pink coloration due to Cu_2C_2 is matched against a titration in an exactly similar flask with standardised C_2H_2 solution (0·02—0·03 c.c. of C_2H_2 per c.c. of H_2O) (accuracy, 4%). Ch. Abs. (*c*)

(A) Reduction of nitro-compounds with liquid zinc amalgam, for analytical purposes. (B) Liquid zinc amalgam method as applied to analysis of nitrobenzaldehydes. M. M. Lobunetz (*Bull. Sci. Univ. Kiev*, 1939, No. 4, 23—36, 41—44).—(A) *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ and *m*- and *p*- but not *o*-nitrocinnamic acid may be determined (error ≯0·5%) by reduction to amines by means of liquid Zn–Hg in dil. H_2SO_4, followed by titration with $KBrO_3$–KBr.

(B) The method is applicable to *m*- but not to *o*- or *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$. R. T.

Iodometric determination of nitrosobenzene. M. M. Lobunetz and E. N. Gortinskaja (*Bull. Sci. Univ. Kiev*, 1939, No. 4, 37—39).—1 g. of PhNO is dissolved in 150 c.c. of EtOH, and H_2O is added to 250 c.c. 30 c.c. of 6N-HCl and 20 c.c. of 20% KI are added to 25 c.c. of solution, and I liberated by the reaction $PhNO + 2HI \rightarrow NHPh{\cdot}OH + 2I$ is titrated. R. T.

Simple method for determination of 2-methyl-1 : 4-naphthaquinol diacetate, a substance exhibiting vitamin-*K* activity. H. Berlin (*Svensk Kem. Tidskr.*, 1940, **52**, 233—238).—The diacetate (I), 15—35 mg., or an Et_2O extract of substances containing ~25 mg. of (I), is dissolved in 20 c.c. of NHAcMe, the temp. adjusted to 18°, 10 c.c. of 2N-NaOH are added, and the time, *t*, required for the development of a red colour is measured. The content of (I) is read from a curve ([A] is approx. ∝ $1/t$). F. J. G.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

FEBRUARY, 1941.

I.—ALIPHATIC.

Synthesis of paraffins. III. Synthesis of paraffins by means of activated adsorption. S. Matsumura, K. Tarama, and S. Kodama (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 181—184B).—The reactions in the synthesis of paraffins from H_2 and CO in presence of Co or Fe are: Co_2C or Fe_2C + adsorbed at. H → $CH_2<$, which polymerises to $C_nH_{2n}<$; reduction of this gives C_nH_{2n+2}, which is adsorbed and liberated by evaporation. The high temp. of initiation of the syntheses are due to low adsorption of H_2 on Co below 160° and the low adsorption of CO on Fe below 190°. W. A. R.

Nitric oxide-inhibited decomposition of ethane.—See A., 1941, I, 51.

Determination of second virial coefficients for seven unsaturated aliphatic hydrocarbons.—See A., 1941, I, 35.

Macropolymerisation; mechanism of activation.—See A., 1941, I, 50.

Catalytic addition of hydrogen chloride to ethylene.—See A., 1941, I, 52.

Allene series. I. Preparation of allene hydrocarbons. J. I. Ginzburg (*J. Appl. Chem. Russ.*, 1940, **10**, 513—516).—$CHCl:C:CMe_2$ or $CMe_2Cl{\cdot}C:CH$ is converted by Zn and Cu in boiling EtOH or BuOH into $CMe_2:C:CH_2$ (62—85% yield). R. T.

Hydrogenation of acetylenic compounds. XXXII. Catalytic hydrogenation of alcohols with double and triple linkings. J. S. Salkind and N. D. Chudekova (*J. Gen. Chem. Russ.*, 1940, **10**, 521—526).—Hydrogenation of $OH{\cdot}CMeEt{\cdot}C:C{\cdot}CH:CH_2$ takes place in three stages (Pd or Pt catalyst), the first product being $OH{\cdot}CMeEt{\cdot}CH:CH{\cdot}CH:CH_2$. This then yields $OH{\cdot}CMeEt{\cdot}CH_2{\cdot}CH_2{\cdot}CH:CH_2$, $OH{\cdot}CMeEt{\cdot}CH:CHEt$, and $OH{\cdot}CMeEt{\cdot}CH_2{\cdot}CH:CHMe$, in approx. equal amounts. The last two atoms of H combine very slowly with these compounds, as compared with the first four H atoms. R. T.

Stabilisation of alkali alcoholates and alcoholic solutions of alcoholates and hydroxides.—See B., 1940, 843.

Decomposition of methyl alcohol at high pressures. A. Apin, O. Leipunski, and N. Reinov (*J. Gen. Chem. Russ.*, 1940, **10**, 863—865).—At 350°/600—8000 atm. the chief reactions are: $2MeOH \rightarrow Me_2O + H_2O$; $Me_2O \rightarrow CH_4 + H_2 + CO$; $MeOH + CO \rightarrow CH_4 + CO_2$; $MeOH + H_2 \rightarrow CH_4 + H_2O$. The velocity of all these reactions rises with increasing pressure. R. T.

Catalytic preparation of ethyl alcohol by the hydration of ethylene. A. Balandin and M. Nesvishski (*Utschen. Zapiski*, 1934, **2**, 233—235; *Chem. Zentr.*, 1935, ii, 1528; cf. A., 1932, 1232).—2% of EtOH is obtained on passing C_2H_4 and H_2O with air over activated C impregnated with 70% H_2SO_4 and Ag_2SO_4 at 150°. The catalyst is readily fatigued. Ch. Abs. (*c*)

Free radicals in the process of pyrolysis and in the electrical discharge. A. Balandin and A. Lieberman (*Utschen. Zapiski*, 1934, **2**, 209—211; *Chem. Zentr.*, 1935, ii, 1525).—The disappearance of a Ag mirror in presence of products of pyrolysing *iso*-$C_5H_{11}{\cdot}OH$ in a quartz tube at 700—800° (modified Paneth–Rice apparatus) indicates the formation of free radicals but at 1100—1200° the mirror is unattacked and a resin is deposited; as also when C_2H_6 is led through a glow discharge. Limitations of this method of detecting free radicals are suggested. Ch. Abs. (*c*)

Isomeric transformations of unsaturated halogen compounds of the aliphatic series. III. Action of hydrochloric acid on methylethylacetylenylcarbinol in presence of ammonium chloride and cuprous chloride. T. A. Favorskaja and A. I. Zacharova. **IV. Action of hydrochloric acid on diethylacetylenylcarbinol in presence of ammonium chloride and cuprous or cupric chloride.** T. A. Favorskaja and I. A. Favorskaja. **V. Reaction of dimethylacetylenylcarbinol with hydrobromic or hydriodic acid.** T. A. Favorskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 446—450, 451—460, 461—467).—III. $OH{\cdot}CMeEt{\cdot}C:CH$ and conc. HCl containing CuCl and NH_4Cl (4 hr. at room temp.) yield *γ-chloro-γ-methyl-*Δ^{α}*-pentine*, b.p. 48—50°/100 mm., with *α-chloro-γ-methyl-*$\Delta^{\alpha\beta}$*-pentadiene*, b.p. 68—70°/100 mm., converted by prolonged contact (8 months) with CuCl and NH_4Cl in HCl into *α-chloro-γ-methyl-*$\Delta^{\alpha\gamma}$*-pentadiene*, b.p. 62—63°/100 mm.

IV. $OH{\cdot}CEt_2{\cdot}C:CH$ and HCl in presence of $CuCl_2$ and NH_4Cl (2 hr. at room temp., then 3 hr. at 50°), yield *α-chloro-γ-ethyl-*Δ^{α}*-pentine* (**I**), b.p. 73—76°/100 mm. When CuCl is used in place of $CuCl_2$, the products are (**I**), *γ-ethyl-*Δ^{α}*-pentin-*Δ^{γ}*-ene* (**II**), b.p. 41—43°/100 mm., and *α-chloro-γ-ethyl-*$\Delta^{\alpha\beta}$*-pentadiene* (**III**), b.p. 85—88°/100 mm. (**II**) is also obtained similarly from (**I**). (**II**) in dil. HCl, in presence of $HgCl_2$, yields $CHMe:CEtAc$, which with p-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2$ affords 2-p-*nitrophenyl*-3 : 5-*dimethyl*-4-*ethylpyrazoline*, m.p. 165—166°.

V. $OH{\cdot}CMe_2{\cdot}C:CH$ and $CuCl_2$ or CuCl in conc. HBr containing NH_4Cl yield *α-bromo-γ-methyl-*$\Delta^{\alpha\gamma}$*-butadiene*, b.p. 48°/42 mm. With HI the product is a mixture of $CMe_2:C:CHI$ and $CH_2:CMe{\cdot}CH:CHI$, decomp. spontaneously at room temp. or during distillation. R. T.

Electrolytic hydrogenation of dimethylvinylacetylenylcarbinol. A. P. Golovtschanskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 435—445).—$CH:C{\cdot}CH:CH_2$ in Et_2O–$COMe_2$ and KOH (4 hr. at 0°) give $OH{\cdot}CMe_2{\cdot}C:C{\cdot}CH:CH_2$ (**I**), in 80% yield. $COMe_2$ is eliminated from (**I**) by boiling with aq. KOH. Electrolytic hydrogenation of (**I**) [Cu cathode, Ni anode; anolyte, saturated aq. NaOH; catholyte, a solution of (**I**) in 3 : 7 EtOH–1% $NaHCO_3$] affords a mixture of $OH{\cdot}CMe_2{\cdot}C:CEt$, $OH{\cdot}CMe_2{\cdot}CH:CH{\cdot}CH:CH_2$, and $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}C:CMe$. R. T.

Tertiary acetylenecarbinols with the acetylenic hydrogen substituted by halogen. T. D. Nagibina (*J. Gen. Chem. Russ.*, 1940, **10**, 427—434).—$OH{\cdot}CMeBu^{\gamma}{\cdot}C:CH$ in light petroleum and aq. KOCl yield *α-chloro-δδ-dimethyl-*Δ^{α}*-pentin-γ-ol* (**I**), b.p. 62—63°/10 mm. (+0·5H_2O, m.p. 38—39°), converted by heating at 100° with 85% HCO_2H into *α-chloro-γ-*tert.*-butyl-*Δ^{α}*-butin-*Δ^{γ}*-ene*, b.p. 25—27°/4 mm.; the corresponding *α-Br*-compound, b.p. 51—52°/6 mm., is prepared analogously. (**I**) and $CuCl_2$ in NH_4Cl–HCl (4 hr. at room temp.) afford *αγ-dichloro-γδδ-trimethyl-*Δ^{α}*-pentine*, b.p. 61—62°/8 mm., m.p. 19—20°. (**I**) and CuCl in NH_4Cl–HCl (36 hr. at room temp.) yield *αα-dichloro-γδδ-trimethyl-*$\Delta^{\alpha\beta}$*-pentadiene*, b.p. 57—58°/11 mm., with some *αα-dichloro-γδδ-trimethyl-*Δ^{α}*-pentene*, b.p. 96—97°/13 mm. R. T.

Action of hypochlorous acid on βε-dimethyl-Δγ-hexine-βε-diol. V. N. Krestinski and N. I. Summ (*J. Gen. Chem. Russ.*, 1940, **10**, 927—934).—$(OH{\cdot}CMe_2{\cdot}C:)_2$ and $NH_2{\cdot}CO{\cdot}NHCl$ (30 hr. at room temp.) yield *γ-chloro-* (**I**), m.p. 85° (*semicarbazone*, m.p. 233°), and *γγ-dichloro-δ-keto-βε-dimethylhexane-βε-diol* (**II**), m.p. 103—104°, and *di-(β-chloro-γ-keto-*$\alpha\alpha\delta$*-trimethyl-*Δ^{δ}*-pentenyl) ether* (**III**), m.p. 122—123°. (**III**) is also obtained from (**I**) and (**II**). (**II**) and NH_2OH yield *γδ-dioximino-βε-dimethylhexane-βε-diol*, m.p. 145—146°. R. T.

Synthesis of asymmetric γ-acetylene glycols. A. T. Babajan (*J. Gen. Chem. Russ.*, 1940, **10**, 480—482).—The reactions $CORR' + KOH + C_2H_2 \rightarrow OK{\cdot}CRR'{\cdot}C:CH$ (**I**); (**I**) + $COR''R''' + KOH \rightarrow OK{\cdot}CR''R'''{\cdot}C:C{\cdot}CRR'{\cdot}OK$ are of

general applicability. C_2H_2 is passed into a suspension of KOH in $COMe_2$–Et_2O (4 hr. at 0°), COMeEt is added, and the mixture is kept for 48 hr. at room temp., and then hydrolysed to a mixture of $(OH\cdot CMe_2\cdot C\equiv)_2$ and *aε-dimethyl-Δ$^\gamma$-heptine-aε-diol*, b.p. 213—216°. The product obtained similarly with $COMePr^a$ in place of COMeEt is *aε-dimethyl-Δ$^\gamma$-octine-aε-diol*, b.p. 222—227°/680 mm., whilst with *cyclo*hexanone it is *α-1-hydroxycyclohexyl-γ-methyl-Δ$^\alpha$-butin-γ-ol*, m.p. 94—95°. (**II**) is in all cases a by-product. R. T.

Thioacetals and related substances. I. Polar effect of sulphur in thioacetals. II. Reaction between α-bromopropaldehyde diethyl acetal and ethylthiol. III. Comparison of the polar effect of sulphur with that of oxygen and nitrogen. E. Rothstein (*J.C.S.*, 1940, 1550—1553, 1553—1558, 1558—1560).—I. $CH_2Cl\cdot CH_2\cdot CH(SEt)_2$, EtSH, AcOH (66%), and HCl give *γ-chloro-aa-di(ethylthiol)propane* (**I**), b.p. 115—117°/11 mm., which with KOH–EtOH affords a mixture of *aa-di(ethylthiol)-Δ$^\alpha$-propene* (**II**), b.p. 83°/9 mm. [oxidised (H_2O_2–AcOH) to *aa-di(ethylsulphonyl)-Δ$^\alpha$-propene* (**III**), m.p. 95·3°], and *γ-ethoxy-aa-di(ethylthiol)propane*, b.p. 115°/9 mm. [oxidised to *γ-ethoxy-aa-di(ethylsulphonyl)propane*, m.p. 35—37°]. With KOBu, (**I**) yields mainly (**II**), in 77% yield, with some *γ-hydroxy-aa-di(ethylthiol)propane*, b.p. 143—145°/10 mm., oxidised to the (*ethylsulphonyl*) compound, m.p. 105—107°; the formation of (**II**) is due to " pinacolic electron displacement " and is enabled to proceed because of the resonance contribution to the transition state of valency structures which can be set up only if the expansion of the S octet is taken into consideration. $HgCl_2$ and (**II**) in MeOH lead to $EtCO_2H$ and an aldehyde forming a 2 : 4-*dinitrophenylhydrazone*, m.p. 149°. BzO_2H and (**II**) in $CHCl_3$ give *αβ-epoxy-aa-di(ethylsulphonyl)propane*, m.p. 75—77°, which with HCl yields a *sulphone*, m.p. 109—110°. $CH_2Br\cdot CHBr\cdot CHO$ and EtSH in C_6H_6 with HCl afford $CH_2Br\cdot CHBr\cdot CH(SEt)_2$, which with Zn gives *aa-di(ethylthiol)-Δ$^\beta$-propene*, b.p. 73°/0·5 mm., also prepared, as well as *γ-chloro-α-ethylthiol-Δ$^\beta$-propene*, b.p. 60—61°/12 mm., from $CH_2{:}CH\cdot CHCl_2$ and NaSEt.

II. From consideration of the hypothesis advanced, it follows that an atom or group which forms a stable anion should be easily eliminated from a mol. in which it was in a β-position to ·SAlk. When $CHMeBr\cdot CH(OEt)_2$ (**IV**) is condensed with EtSH, AcOH, and HBr at 0°, followed by distillation, HBr is eliminated and *αβ-di(ethylthiol)-Δ$^\alpha$-propene* (**V**), b.p. 88—97°/9 mm., is formed, which is oxidised to the -(*ethylsulphonyl*) compound (**VI**), m.p. 73—74°. Boiling a xylene solution of the mixture gives *aaβ-tri(ethylthiol)propane*, b.p. 100°/0·3 mm., oxidised to the *sulphone*, m.p. 114—115°, (**III**), and (**VI**), and by treatment with aq. $HgCl_2$ forming *α-ethylthiolpropaldehyde*, b.p. 34—37°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 95—96°), and AcCHO [the 2 : 4-dinitrophenylosazone is not identical with *malonaldehydebis-2 : 4-dinitrophenylhydrazone*, m.p. 284° (decomp.)]. A $CHCl_3$ solution of (**V**) is ozonised to a *sulphide*, b.p. 115—118°/9 mm. *β-Ethylthiolpropaldehyde Et$_2$ acetal*, b.p. 94—97°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 107°), prepared from the corresponding Cl-compound, with EtSH and AcOH–HCl gives *aaγ-tri(ethylthiol)propane*, b.p. 87°/0·2 mm., oxidised to the *-sulphonyl* compound, m.p. 105—106°. *α-Ethylthiolpropaldehyde Et$_2$ acetal*, b.p. 78—80°/9 mm., is obtained in small yield from the corresponding α-Br-compound. *α-n-Butylthiolpropaldehyde*, b.p. 71·5—72·5°/9 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 107—109°), prepared from BuSH, NaOEt, and $CHMeBr\cdot CHO$, with EtSH and AcOH–HCl affords *aa-di(ethylthiol)-β-n-butylthiolpropane*, b.p. 114—116°/0·3 mm., oxidised to (**III**) and *α-ethylsulphonyl-β-n-butylsulphonyl-Δ$^\alpha$-propene*, m.p. 52°, and yielding on treatment with KOBu$^\gamma$ Bu^aSH, identified as *Hg dibutylthiol*. *aaγ*-Tri(ethylthiol)-propane is stable under conditions whereby an SEt group is removed from the *aaβ*-derivative.

III. $OH\cdot[CH_2]_3\cdot NMe_3Cl$ (*picrate*, m.p. 158—159°) with $SOCl_2$ gives the γ-Cl-compound (*picrate*, m.p. 132—134°), which with NaOEt is converted into the allyl compound (*picrate*, m.p. 214—215°); the Δ$^\alpha$-unsaturated compound is not formed, in accordance with the theory put forward. Similarly the action of KOBu$^\gamma$ on $CH_2Cl\cdot CH_2\cdot CH(OEt)_2$ yields acraldehyde acetal and an acetal forming a 2 : 4-*dinitrophenylhydrazone*, m.p. 78—79°, and not methylketen acetal. These results are to be expected since N and O cannot expand the outer valency shell. F. R. S.

Influence of poles and polar linkings on tautomerism in the simple three-carbon system. VI. Unbalanced systems. E. Rothstein (*J.C.S.*, 1940, 1560—1565).—$CHMeCl\cdot CH_2\cdot NMe_3Cl$ (*picrate*, m.p. 161—162°) with KOH–EtOH gives the *-Δ$^\alpha$-propenyl picrate*, m.p. 170—172°, when kept for some hr. at room temp., and when boiled for 20 min. yields a *NNNN'N'N'*-hexamethylenediammonium salt (*picrate*, m.p. 315—316°). The Δ$^\alpha$-isomeride showed no tendency to be converted into the allyl compound, mobility of the system depending on similarity of constitution of the two isomerides. Ozonolysis of $CHMe{:}CH_2\cdot NMe_3Cl$ affords MeCHO and a substance forming a *picrate*, m.p. 189°. Acraldehyde, EtSH, and $ZnCl_2$ in CCl_4 yield a mixture of *β-ethylthiolpropaldehyde*, b.p. 60°/10 mm., *aaγ*-tri(ethylthiol)propane, and an unidentified fraction, b.p. 160—170° (decomp.)/0·5 mm. The action of alkali on *γ-chloro-*, m.p. 96—97°, or *γ-iodo-aa-di(ethylsulphonyl)propane*, m.p. 95° (prepared from the *γ-OEt*-compound, m.p. 35—37°), gives 1 : 1-*di(ethylsulphonyl)*cyclo*propane* (**I**), m.p. 131—132°. Oxidation (30% H_2O_2) of the product from dibromopropaldehyde and EtSH affords a small amount of *γ-bromo-aa-di(ethylsulphonyl)-Δ$^\beta$-propene* (?), m.p. 102°. *αβ-Dimethoxypropaldehyde Et$_2$ acetal*, b.p. 83—85°/10 mm., with EtSH gives *βγ-dimethoxy-aa-di(ethylthiol)propane*, b.p. 129—130°/8 mm., oxidised to *γ-hydroxy-β-methoxy-aa-di(ethylsulphonyl)propane*, m.p. 108°. Distillation of trimethyl-γγ-di(ethylsulphonyl)propylammonium hydroxide with EtSH followed by treatment with picric acid leads to the -(*ethylthiol*) *picrate*, m.p. 94°, which is oxidised to (**I**). The foregoing methods were attempts to prepare aa-di(ethylsulphonyl)-Δ$^\beta$-derivatives.

aa-Di(ethylsulphonyl)-Δ$^\alpha$-propene is stable to heat and can be distilled without change; with Br it forms a *dibromide*, with NaOMe it gives a *sulphone*, $C_9H_{16}O_4S_2$, but with NaOMe–MeI, a *sulphone*, $C_{15}H_{30}O_8S_4$, m.p. 162°, is obtained and this is oxidised (O_3) to a *di(ethylsulphonyl)-propionic acid*, m.p. 131°. F. R. S.

Organic selenium compounds. Their decomposition in alkaline solutions and their properties related to the behaviour of selenium compounds in cereals. E. P. Painter, K. W. Franke, and R. A. Gortner (*J. Org. Chem.*, 1940, **5**, 579—589).—The prep. of $(Se\cdot CH_2\cdot CO_2H)_2$ (**I**), m.p. 100°, $(\cdot Se\cdot CH_2\cdot CH_2\cdot CO_2H)_2$ (**II**), m.p. 134·5—135·5°, and $Pr^a{}_2S_2$ (**III**) is reported. K_2S_2 and CH_2PhCl in aq. EtOH at 100° afford *dibenzyl diselenide*, m.p. 92—93°. $Br\cdot[CH_2]_2\cdot CO_2K$ and K_2S give *β-selenodipropionic acid* (**IV**), m.p. 147—148°. *Dibenzyl selenide* has m.p. 45°. Addition of 30% H_2O_2 to (**I**) in Et_2O gives a 90% yield of *seleninoacetic acid*, $CO_2H\cdot CH_2\cdot SeO_2H$, m.p. 101°. *β-Seleninopropionic acid*, m.p. ~106° (decomp.), is obtained similarly in $COMe_2$. *n-Propylseleninic acid*, obtained by oxidising (**III**) with conc. HNO_3, gives a *compound*, $PrSeO_2H,HNO_3$, m.p. 98°. The corresponding substance, $CH_2Ph\cdot SeO_2H,HNO_3$, could not be obtained pure. Se compounds appear less stable in air and in neutral solutions than the corresponding S compounds. Most are stable in neutral org. solvents. The diselenides of org. acids decompose slowly giving metallic Se after they have aged for several days or weeks. (**II**) decomposes much more rapidly than (**I**). Se ethers appear stable, no decomp. being noticeable after several months. The acids decompose rapidly in H_2O and in air, giving metallic Se and diselenide. Diselenides, like disulphides, decompose in alkaline solution giving inorg. selenide and selenite. Se ethers, like S ethers, are stable but (**IV**) is decomposed in alkaline plumbite to give nearly all the Se as PbSe. Se from seleninic acids of org. acids appears to be quantitatively cleaved whilst the seleninic acids of hydrocarbons are partly cleaved, selenide and PbSe being formed. The mechanism of decomp. of these compounds is probably identical with that of the corresponding S compounds.

The relationship of Se compounds in plants and synthesised compounds in regard to their stability in different solutions and on storage is discussed. H. W.

Thermal decomposition of nickel formate.—See A., 1941, I, 51.

Inhibiting action of some asymmetric organic acids on asymmetric oxidation.—See A., 1941, I, 52.

***iso*Propyl and *iso*butyl acrylates.** A. V. Ipatov (*J. Gen. Chem. Russ.*, 1940, **10**, 866—868).—*Pr$^\beta$*, b.p. 108—112°, and *Bu$^\beta$ acrylate*, b.p. 130—134°, were prepared by the reactions $CH_2Br\cdot CHBr\cdot CO_2R + Zn \rightarrow CH_2{:}CH\cdot CO_2R + ZnBr_2$ or $OH\cdot[CH_2]_2\cdot CN + ROH + H_2SO_4 \rightarrow CH_2{:}CH\cdot CO_2R + NH_4HSO_4$. R. T.

Kinetics of the olefine–bromine reaction.—See A., 1941, I, 51.

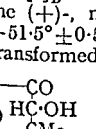
Hydrogenation and exchange reactions of methyl oleate. J. H. Baxendale and E. Warhurst (*Trans. Faraday Soc.*, 1940, **36**, 1181—1188).—Me oleate is treated with D_2 in presence of Pt-black at 170°, and the products of the incomplete reaction, as well as their oxidation ($COMe_2$–$KMnO_4$) products, are examined quantitatively. Exchange of D with H on saturated C atoms is inappreciable. "Heavy" products (oleic, elaidic, and *cis*- and *trans*-esters with the double linking shifted to the Δ^7 or Δ^4 positions) are formed in small quantities only, the main product being "light" *trans*-esters. These results cannot be accounted for by any dissociative mechanism, nor do they provide positive evidence for the associative mechanism discussed by Greenhalgh and Polanyi (A., 1939, I, 322). A mechanism which would lead to the production of "light" *trans*-products, and is at the same time reconcilable with the association hypothesis, is proposed.

F. L. U.

Formation of carbonic and carboxylic esters. E. Baur and M. Namek (*Helv. Chim. Acta*, 1940, **23**, 1101—1110).—Photodynamic pigments which contain CO_2Alk give CH_2O under definite conditions in light. Probably CH_2O is derived from CO_2H of the pigment resulting from decarboxylation and consequent liberation of the alcohol. The re-formation of the pigment requires the reactions, $ROH + CO_2 = OR{\cdot}CO_2H$ (**I**) and $R'H + (I) = R'{\cdot}CO_2R + H_2O$. These reactions can be observed separately. The absorption of CO_2 by H_2O, Bu_2O, or octane is complete within 10 min. and thereafter there is no further change during many days. With alcohols there is a rapid initial physical absorption followed by a much slower chemical absorption which is attributed to the formation of alkyl carbonates. Physical and chemical absorption are not parallel phenomena. Much physical and little chemical absorption is observed with EtOH; the reverse is the case with glycerol (**II**). The chemical absorption varies between 1 mol. per thousand and 2 mol.-%. Max. vals. are observed with (**II**), phytol, and cetyl alcohol. As expected, CO_2 expedites hydrolysis of glycerides and waxes; cottonseed oil, lecithin, and cetyl palmitate are placed in order of increasing action. The absorption of CO_2 in (**II**), EtOH, or BuOH is increased by the presence of phloroglucinol but the phloroglucinolcarboxylic ester could not be isolated. A similar effect is caused by rosolic acid in (**II**) or BuOH and the product is fluorescent in H_2O, doubtless owing to carboxylation.

H. W.

Crystalline quinine salts of (+)- and (−)-pantothenic acid and the biological activity of ethyl *d*(+)-pantothenate. A. Grüssner, M. Gätzi-Fichter, and T. Reichstein (*Helv. Chim. Acta*, 1940, **23**, 1276—1286).—*dl*-α-Hydroxy-ββ-dimethylbutyrolactone is boiled with $Ba(OH)_2$ in MeOH and the solution is treated successively with CO_2 and quinine sulphate whereby quinine salts of the crude (+) and (−) acids are obtained. These are re-converted into the Ba salts, which are purified from H_2O–$COMe_2$. Thus are obtained *Ba* (+)-, m.p. 198—200° (decomp.), $[\alpha]_D^{19}$ +5·5°±1° in H_2O, *Ba* dl-, m.p. 220° (corr.; decomp.), and *Ba* (−)-, m.p. 198—200° (corr.; decomp.), $[\alpha]_D^{20}$ −6·5±1·5° in H_2O, -salts. The requisite salts are transformed by HCl–EtOH into the (−)-, m.p. 89—90°, $[\alpha]_D^{17}$ −17·4°±0·5° in $COMe_2$, $[\alpha]_D^{17.5}$ −49°±0·5° in H_2O, and the (+)-, m.p. 89—90°, $[\alpha]_D^{18}$ +14·5°±0·5° in $COMe_2$, $[\alpha]_D^{17}$ +51·5°±0·5° in H_2O, -lactone. The former compound is transformed by $NHPh{\cdot}NH_2$ at 100° into d-α*γ*-*dihydroxy*-ββ-*dimethylbutyrphenylhydrazide*, b.p. 155° (bath)/0·01 mm., $[\alpha]_D^{18}$ +33·2°±1° in EtOH, so that it has the configuration (*A*) if Hudson's rules are applicable to this compound. *Et* d(+)-*pantothenate* has b.p. 135—140°/0·01 mm., $[\alpha]_D^{18}$ +36·8°±0·5° in abs. EtOH, whereas $[\alpha]_D^{19}$ −37·3°±1° in abs. EtOH is recorded for the l(−)-*ester*. *Quinine* d(+)-*pantothenate* (*monohydrate*, m.p. 136—137°, $[\alpha]_D^{19}$ −95°±2° in H_2O), and l(−)-*pantothenate*, m.p. 183—183·5°, $[\alpha]_D^{18}$ −121°±2° in H_2O, are characteristic.



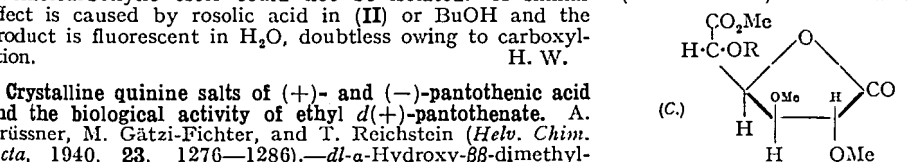
(*A.*)

[With H. Pfaltz.] The biological action of the acids is described, particularly in regard to growth-promoting properties; the *d*(+)-acid esters are much more active in this respect than those of the *l*(−)-acid, which, indeed, are in many cases almost inactive.

H. W.

Constitution of arabic acid. V. Methylated arabic acid. F. Smith (*J.C.S.*, 1940, 1035—1051).—Gum arabic or arabic acid (**I**) is treated with Me_2SO_4–NaOH, followed by remethylation of the resulting Na salt, with addition of $COMe_2$. After 6—10 methylations, *methylated arabic acid* (**II**), $[\alpha]_D^{18}$ −47° in $CHCl_3$, is obtained, apparently essentially homogeneous. This with CH_2N_2 in Et_2O, followed by Purdie methylation, gives its *Me* ester (**III**), $[\alpha]_D^{24}$ −48° in $CHCl_3$. Attempted hydrolysis of (**II**) by dil. HCl causes decomp., with formation of CO_2 and reductinic acid. With boiling 4% MeOH–HCl, (**III**) undergoes hydrolysis and glycoside formation, the seven glycosides (**VIII**), (**IX**), (**XIII**)—(**XVI**), and (**XIX**) (see below) being formed. The mixture with 0·3N-$Ba(OH)_2$ at 60° gives an Et_2O-insol. Ba salt (**IV**), and a mixture of methylated glucosides sol. (**V**) and insol. (**VI**) in light petroleum.

H_2SO_4–$PbCO_3$–H_2S converts (**IV**) into 2 : 3-*dimethylmethylglucuronoside* (**VII**) (*A*; R = R′ = H), $[\alpha]_D^{18}$ +68° in H_2O {which when distilled gives no lactone, but an acid [identical with (**VI**) (?)], b.p. 186° (bath)/0·03 mm., $[\alpha]_D^{18}$ +65° in H_2O}, which with boiling MeOH–HCl forms its *Me* ester (**VIII**) (*A*; R = H, R′ = Me), b.p. 145° (bath)/0·04 mm., $[\alpha]_D^{18}$ +76° in H_2O (p-*nitrobenzoate*, m.p. 157°), and the Me ester (**IX**) (*A*; R = R′ = Me), b.p. 125° (bath)/0·03 mm., $[\alpha]_D^{18}$ +85° in H_2O, of 2 : 3 : 4-trimethylmethylglucuronoside. With $NHPh{\cdot}NH_2$ at 110°, (**VIII**) gives the *phenylhydrazide*, m.p. 225—227°, of (**VII**). As the glucuronic acid residues of degraded (**I**) have pyranose structures, so must the corresponding uronic acid residues which furnish (**VII**) and (**VIII**). Thus neither Me can be in the 5-position, and (**VII**) and (**VIII**) have 2 : 3-, 2 : 4-, or 3 : 4-Me_2. (**VIII**) is hydrolysed [$Ba(OH)_2$, H_2SO_4] to (**VII**), and this (dil. H_2SO_4 at 100°; $BaCO_3$) to the Ba salt of 2 : 3-dimethylglucuronic acid (*B*). This salt is oxidised (Br–H_2O, followed by Ag_2O and H_2S) to the acid Ba salt of 2 : 3-dimethylsaccharic acid, which with 4% MeOH–HCl at the b.p. gives 2 : 3-*dimethylsaccharo*-γ-*lactone Me ester* (**X**) (*C*; R = H), m.p. 190° (bath)/0·03 mm., $[\alpha]_D^{18}$ +12·0° in H_2O (see also below). This is also obtained [with (**XII**), below] by



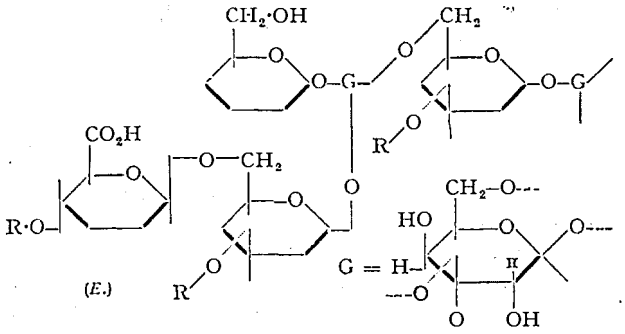
(*A.*) (*B.*)

oxidising (**VIII**) with HNO_3 (*d* 1·42) at 50—95°, followed by esterification (1% MeOH–HCl; Ag_2CO_3) and distillation. That (**X**) is a γ-lactone is indicated by its relatively slow hydrolysis in H_2O ($[\alpha]_D^{22}$ +14° → +20·6° in 4 days → +27·7° in 10 days), and confirmed by methylation (Ag_2O–MeI) of (**X**) to 2 : 3 : 5-*trimethylsaccharo*-γ-*lactone Me ester* (**XI**) (*C*; R = Me), m.p. 78°, $[\alpha]_D^{20}$ −10° in H_2O. The constitution of this follows from its prep. by oxidation of 2 : 3 : 5-trimethylmethylglucofuranoside by HNO_3, followed by esterification and distillation. The presence of the 1 : 4-lactone ring in (**X**) and (**XI**) shows that (**VIII**) has free OH at $C_{(4)}$ and thus 2 : 3-Me_2. This is confirmed by HNO_3 oxidation (followed by esterification) of both (**VIII**) and (**X**) to the Me ester of *l*(+)-threodimethoxysuccinic acid (*d*-dimethoxysuccinic acid) (**XII**) (*D*), identified as the *diamide*, m.p. 293° (decomp.), $[\alpha]_D^{18}$ +90° in H_2O. Further, synthetically, 4 : 6-benzylidene-α-methylglucoside gives (Purdie) its 2 : 3-Me_2 derivative, which in N-H_2SO_4, followed by $BaCO_3$, yields 2 : 3-dimethylglucose, and (1% MeOH–HCl) 2 : 3-dimethylmethylglucoside, which in HNO_3, followed by esterification, gives (**X**) and the ester of (**XII**). Attempted prep. of (**X**) from 2 : 3 : 6-trimethylglucono-δ-lactone by HNO_3 oxidation gives (**XII**). Purdie methylation of (**VIII**) gives (**IX**), identified by conversion (MeOH–NH_3) into 2 : 3 : 4-trimethyl-*d*-methylglucuronoside (cf. A., 1940, II, 5); the 2 : 3 : 4-Me_3 structure of (**IX**) is also shown by its hydrolysis by dil. H_2SO_4 to 2 : 3 : 4-trimethylglucuronic acid, oxidised by Br to the corresponding saccharic acid, identified as 2 : 3 : 4-trimethylsaccharo-δ-lactone Me ester.

The mixture (**V**) contains 2 : 3 : 5-trimethylmethylarabino-

(furano)side (**XIII**), 2 : 3 : 4-trimethylmethylrhamno(pyrano)-side (**XIV**), 2 : 3 : 4 : 6-tetramethylmethylgalactoside (**XV**), and 2 : 5-dimethylmethylarabinoside (**XVI**). Separation of (**V**) into its constituents cannot be effected by fractional distillation, since (**XIII**) and (**XIV**) form a mixture of const. b.p., as do (**XV**) and (**XVI**). 0·1N-H_2SO_4 hydrolyses both (**XIII**) and (**XIV**) and effects no separation; the presence of 2 : 3 : 4-trimethylrhamnose in the hydrolysate is confirmed by the prep. of its anilide. The hydrolysate is oxidised by Br to a mixture of lactones containing 2 : 3 : 4-trimethylrhamnonic acid (phenylhydrazide) and 2 : 3 : 5-trimethylarabonic acid (amide). Hydrolysis of (**XV**) + (**XVI**) by 0·1N-H_2SO_4 gives unchanged (**XV**) [hydrolysed (N-H_2SO_4) to 2 : 3 : 4 : 6-tetramethylgalactose (**XVII**), which gives its anilide (**XVIII**)], and a const.-boiling mixture of 2 : 5-dimethylarabinose and (**XVII**). This mixture with EtOH–NH_2Ph gives (**XVIII**). Oxidation (Br) gives 2 : 3 : 4 : 6-tetramethylgalactonic acid (phenylhydrazide) and 2 : 5-dimethylarabonic acid (phenylhydrazide; amide). Hydrolysis of heptamethyl-3-galactosido-*l*-arabofuranose with boiling MeOH–HCl gives a mixture of the methylated glycosides, and this (N-H_2SO_4) a mixture of sugars, with similar properties to the above mixture. The presence of (**XVI**) is also shown by completely hydrolysing (**V**) (N-H_2SO_4, 10 hr.; $BaCO_3$) to a reducing methylated sugar, which after extraction by light petroleum, and treatment with 1% MeOH–HCl to const. [α], neutralisation, distillation, hydrolysis, and oxidation (Br) gives 2 : 5-dimethylarabono-γ-lactone. The residue (**VI**) consists of α- and β-forms of 2 : 4-dimethylmethylgalactoside (**XIX**) (cf. *loc. cit.*), both hydrolysed (N-H_2SO_4) to the same 2 : 4-dimethylgalactose, oxidised to 2 : 4-dimethylgalactono-δ-lactone.

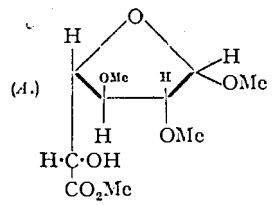
The identification of the products from (**III**) shows the branched structure of (**I**), and shows that *l*-arabinose (**XX**), *l*-rhamnose, and 3-galactopyranosido-*l*-arabinose, liberated in the autohydrolysis of (**I**), are joined to the nucleus of degraded (**I**) in the form of *l*-arabofuranose (**XXI**), *l*-rhamnopyranose (**XXII**), and 3-galactopyranosido-*l*-arabofuranose (**XXIII**). In addition to the 1 : 3- and 1 : 6-linkings in (**I**), isolation of (**VIII**) shows the presence of a 1 : 4-linking. The repeating structure (*E*), in which the residues R consist of (**XXI**), (**XXII**), and (**XXIII**), is proposed for (**I**).

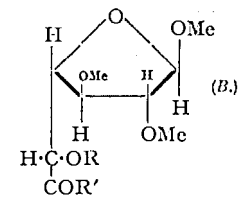


(*E.*)

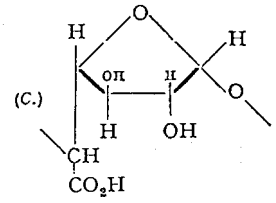
The mixture of reducing sugars obtained from (**I**) by autohydrolysis freed as far as possible from (**XX**) (cf. A., 1939, II, 298), dissolved in MeOH, and evaporated (room temp.; 18 months) gives crystals of *l*-rhamnose hydrate, which are separated by hand. 2 : 3 : 5-Trimethyl-*l*-rhamnono-γ-lactone with NHPh·NH_2 in Et_2O gives 2 : 3 : 5-*trimethyl-l-rhamnon-phenylhydrazide*, m.p. 160°. E. W. W.

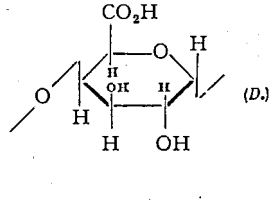
Constitution of pectic acid. I. Methylation of pectic acid, and isolation of the methyl ester of 2 : 3-dimethylmethyl-galacturonoside. II. Synthesis of the methyl ester of 2 : 3 : 5-trimethyl-β-methylgalacturonoside. (Miss) S. Luckett and F. Smith (*J.C.S.*, 1940, 1106—1114, 1114—1118).—I. Pectic acid (**I**) from citrus pectin, corresponding with Ehrlich's " tetragalacturonic acid " (A., 1933, 491), when boiled in H_2O hydrolyses to give ultimately galacturonic acid. The partly degraded product is converted by MeOH–HCl at room temp., followed by Purdie methylation, into the Me ester of 2 : 3 : 4-trimethyl-α-methylgalacturonoside. When repeatedly treated with Me_2SO_4–NaOH, (**I**) gives a partly methylated product, purified by addition of H_2SO_4 and dialysis. After renewed methylation, and treatment of the Th (or Ag) salt with MeI–MeOH, the product is methylated (Purdie), and after fractional pptn. in $COMe_2$ by Et_2O gives the *Me* ester (**II**), $[\alpha]_D^{20}$ +223·5° in H_2O, of *methylated pectic acid*. 1% MeOH–HCl at the b.p. causes only slight hydrolysis of (**II**), but at 120° gives the *Me* ester (**III**), b.p. 120—125° (bath)/0·04 mm., $[\alpha]_D^{15}$ −64° in H_2O, of 2 : 3-*dimethylmethylgalactofururonoside* (**IV**), with a methylmethylgalacturonoside (cf. A., 1939, II, 242). Formula (*A*) is assigned to (**III**), which with MeOH–NH_3 gives the *amide* (*B*; R = H, R′ = NH_2), m.p. 124°, $[\alpha]_D^{17}$ −151° in H_2O, of 2 : 3-dimethyl-β-methylgalactofururonoside.


(*A.*)


(*B.*)

Purdie methylation of (**III**) gives the *Me* ester (**V**) (*B*; R = Me, R′ = OMe) (for synthesis, see below), m.p. 42°, $[\alpha]_D^{12}$ −123° in MeOH, of 2 : 3 : 5-*trimethyl-β-methylgalactofururon-oside* (**VI**), converted by MeOH–NH_3 (−5°; 2 days) into the *amide* (*B*; R = Me, R′ = NH_2), m.p. 106°, $[\alpha]_D^{14}$ −151·5° in H_2O. In HNO_3 (*d* 1·42) at 50—80°, (**V**) gives the *γ-lactone Me ester* (**VII**), m.p. 62°, b.p. 160° (bath)/0·01 mm., $[\alpha]_D^{20}$ −83° in H_2O, of βγε-trimethylmucic acid (**VIII**). In MeOH–NH_3 (room temp.; 2 days), (**VII**) gives the *diamide* (**IX**), m.p. 255° (decomp.), of (**VIII**). Hydrolysis of (**III**) by 0·244N-$Ba(OH)_2$ gives the Ba salt, which with N-H_2SO_4 at 100° yields, fairly slowly ($[\alpha]_D$ −41° → +80° in 24 hr.) [suggesting that a furanoside ring is present in (**IV**) and therefore in (**III**)] a dimethylgalacturonic acid. This is oxidised by Br to an acid which is esterified to the *γ-lactone Me ester* (**X**), m.p. 92°, b.p. 160—165° (bath)/0·02 mm., $[\alpha]_D^{17}$ −55·8° → −4° in H_2O, of βγ-dimethylmucic acid (**XI**). That (**X**) contains a 1 : 4-γ-lactone ring is shown by Purdie methylation to (**VII**) (with Me βγδε-tetramethylmucate), which is synthesised (below). (**X**) is also obtained by oxidising (**III**) by HNO_3 (*d* 1·42) and esterifying the resulting (**XI**). (**VII**) and (**IX**) are enantiomorphs of the 3 : 6-γ-lactone Me ester of βδε-trimethylmucic acid and its diamide (cf. A., 1940, II, 5): $C_{(4)}$ in (**III**) thus does not carry OMe. In MeOH–NH_3, (**X**) forms the *diamide* (**XII**), m.p. 228° (decomp.), of (**XI**), and in MeOH–NH_2Me the corresponding *bismethylamide* (**XIII**), m.p. 184°, $[\alpha]_D^{17}$ −7·5° in H_2O. With NaOCl, (**XII**) undergoes a Weerman degradation with formation of NaNCO; there must thus be free OH at $C_{(2)}$ or $C_{(5)}$. The 2 : 3-position of Me_2 is confirmed synthetically. 2 : 3-Dimethylgalactose (Robertson *et al.*, A., 1934, 1206) in HNO_3 (*d* 1·42; 55—75°), followed by boiling 1% MeOH–HCl, Ag_2CO_3, and distillation, gives (**X**), from which (**XII**) and (**XIII**) are prepared as before. It is thus shown that (**I**) is composed of galacturonic acid residues joined by linkings not involving positions (2) and (3). The alternative repeating units (*C*) and (*D*) are possible. Although (**III**) has a furanose structure, this may


(*C.*)


(*D.*)

not pre-exist in (**I**), and the high [α] of (**I**) and (**II**) favour the unit (*D*). Thus in respect of its glycosidic linkages, (**I**) resembles starch and not cellulose. Osmotic pressure indicates that (**II**) has a mol. size of ~13 units. As a terminal group (the Me ester of a trimethylmethylgalacturonoside) is not detected in cleavage products, (**II**) may consist of galacturonic acid residues arranged loop-wise. Aq. *dl*-γ-lactone Me ester of trimethylmucic acid, with Me_2SO_4–NaOH, gives a product esterified (1% MeOH–HCl) to *Me βγδε-tetramethylmucate*, m.p. 109°, [α] 0°.

II. Methylgalactofuranoside (cf. Haworth *et al.*, A., 1925, i, 117) in C_5H_5N gives its 6-*CPh*$_3$ *ether*, $[\alpha]_D^{18}$ −33° in $COMe_2$, which on repeated methylation by Me_2SO_4–NaOH in $COMe_2$ gives the 6-*CPh*$_3$ *ether*, $[\alpha]_D^{15}$ −19° in $CHCl_3$, of 2 : 3 : 5-*tri-methylmethylgalactofuranoside* (**XIV**), b.p. 150° (bath)/0·05 mm., $[\alpha]_D^{18}$ −55° in H_2O (isolated by use of Et_2O–HCl and $PbCO_3$). The last with 0·1N-H_2SO_4 at 100° (bath) gives

2 : 3 : 5-*trimethylgalactose*, $[\alpha]_D^{15}$ −5° in H_2O, oxidised by Br–H_2O, followed by Ag_2O and H_2S, to 2 : 3 : 5-*trimethylgalactono-γ-lactone*, m.p. 90°, $[\alpha]_D^{18}$ −37° → −32° (5 days, incomplete) in H_2O, which with MeOH–NH_3 at −5° forms the *amide*, m.p. 152°, $[\alpha]_D^{16}$ +3° in H_2O, and with NHPh·NH_2 the *phenylhydrazide*, m.p. 144°, $[\alpha]_D^{14}$ +18° in EtOH, of *βγε*-trimethylgalactonic acid. With $KMnO_4$–KOH, followed by H_2SO_4 and evaporation, (**XIV**) gives a residue from which $CHCl_3$ extracts (**VI**), of which the Ba salt with 1% MeOH–HCl (8 hr.) yields (**V**) (which gives the amide as before), as a mixture of the α- with the cryst. *β-form* (**XV**). In HNO_3 (*d* 1·42; 50—80°), (**XIV**) or (**XV**) gives (**VII**). With MeOH–NH_3 (−5°; 3 days) (**VII**) yields (**IX**) as before; intermediately the *amide*, m.p. 173°, of the Me_1 ester of (**VII**) is obtained. In MeOH–NH_2Me (room temp.; 3 days), (**VII**) forms the *bismethylamide*, m.p. 232°, $[\alpha]_D^{17}$ −22° in H_2O, of (**VIII**). The furanoside structure of (**XIV**) and (**XV**) is confirmed by the fact that (**IX**) gives a negative Weerman test for α-hydroxyamide.

E. W. W.

Constitution of pectic acid. HI. Hydrolysis of the methyl ester of methylated pectic acid and isolation of the methyl ester of 2 : 3-dimethyl-β-methylgalactopyruronoside. (Miss) S. Luckett and F. Smith (*J.C.S.*, 1940, 1506—1511; cf. preceding abstract).—Prolonged boiling of the Me ester of methylated pectic acid with 2% MeOH–HCl yields the *Me* ester (**I**), m.p. 111°, $[\alpha]_D^{17}$ −11° in H_2O, of 2 : 3-dimethyl-β-methylgalactopyruronoside. Hydrolysis (1% HNO_3), oxidation (HNO_3, *d* 1·42), esterification (CH_2N_2), and distillation of (**I**) yields the γ-lactone of Me βγ-dimethylmucate. Methylation (MeI–Ag_2O) of (**I**) yields the *Me* ester of 2 : 3 : 4-trimethyl-β- (**II**), m.p. 102°, $[\alpha]_D^{18}$ −20° in MeOH, converted by 2% MeOH–HCl at 100° under pressure into 2 : 3 : 4-trimethyl-α-methylgalactopyruronoside Me ester. The latter (prepared by methylation of α-methylgalactopyruronoside) on hydrolysis (dil. H_2SO_4) and methylation (Me_2SO_4) yields (**II**). Methylation (Me_2SO_4) of 6-triphenylmethyl-β-methylgalactoside yields 6-*triphenylmethyl*-2 : 3 : 4-*trimethyl-β-methylgalactopyranoside*, $[\alpha]_D^{17}$ −23° in $CHCl_3$, hydrolysed (Et_2O–HCl) to 2 : 3 : 4-*trimethyl-β-methylgalactopyranoside* (**III**), m.p. 70—72°, $[\alpha]_D^{18}$ +11° in H_2O, methylated (MeI–Ag_2O) to the 2 : 3 : 4 : 6-tetramethylgalactoside, and converted by hydrolysis (N-H_2SO_4) and treatment with NH_2Ph into 2 : 3 : 4-trimethylgalactose anilide. Oxidation (KOH–$KMnO_4$) and esterification (CH_2N_2) of (**III**) yields (**II**).

A. Li.

Manufacture of formaldehyde.—See B., 1940, 843.

Composition of the Ponndorff–Meerwein reduction product of mesityl oxide. J. Kenyon and D. P. Young (*J.C.S.*, 1940, 1547—1550).—Reduction of mesityl oxide (**I**) with $Al(OPr^{\alpha})_3$ gives *αγγ*-trimethylallyl alcohol (**II**) (p-*xenylurethane*, m.p. 94°, identical with that prepared from an authentic specimen) and some δ-methyl-Δ^{δ}-penten-β-ol, recognised by the formation of its H phthalate. This is held to confirm the conclusion of Dupont and Menut (A., 1939, II, 402) that (**I**) contains a significant amount of CH_2:CMe·CH_2·COMe. Catalytic dehydration (small quantity of I) affords the abnormal product, CHMe:CH·CHMe:CH_2, the course of the reaction apparently being dependent on the experimental conditions. F. R. S.

Di-imides of enolisable diketones and dialdehydes. G. Schwarzenbach and K. Lutz (*Helv. Chim. Acta*, 1940, **23**, 1139—1146).—The great stability of the imides of enolisable diketones and dialdehydes is related to mesomerism. The di-imides of glutacondialdehyde have a chain of three conjugated double linkings and yield salts the cation of which can be expressed by two limiting formulæ of the mesomeric particle. Since these are identical, the cation is a so-called symmetrical resonance system resembling C_6H_6. Symmetrical resonance systems are invariably remarkably stable since they have a high resonance energy which stabilises the otherwise unstable imide. Only the salts are stable whereas the bases are unsymmetrical and readily hydrolysed. 2′ : 4′-Dinitrophenylpyridinium chloride is converted by NH_2Et at room temp. into glutacondiethylimide (isolated as the *perchlorate*, decomp. 99°) and 2 : 4 : 1-$(NO_2)_2C_6H_3$·NH_2. *Glutacondiisobutylimide perchlorate* is described. CH_2Ac_2 is transformed by anhyd. NH_2Et into the monoethylimide, b.p. 91°/15 mm., converted by anhyd. NH_2Et and AcOH at 100° into acetylacetonediethylimide, isolated as the *perchlorate*, m.p. 167·5°. CH_2Ac_2 and $(CH_2$·$NH_2)_2$ give the amphoteric compound $(CH_2$·NH·CMe:CHAc$)_2$, m.p. 111·5°, but if AcOH is gradually added to these reactants heated at 120° the product is the stable 2 : 7-*dimethyl*-3 : 6-*diaza*-$\Delta^{1:6}$-*cycloheptadiene* (*perchlorate*, m.p. 140°). Dihydroresorcinol is transformed by NH_2Ph and AcOH at ~180° followed by $NaClO_4$ into dihydroresorcinoldianil perchlorate, m.p. 218·5°. Dimedon and NH_2Et in EtOH give the monoethylimide, m.p. 118°, transformed by 33% NH_2Et and AcOH at 180° into *dimedondiethylimide perchlorate*, m.p. 75·5°. Similar processes lead to *dimedondidimethylaminoanil hydrochloride*, m.p. >280°, and *dimedondi*-p-*hydroxyanil hydrochloride*, m.p. >280°. H. W.

2-Aldopolyhydroxyalkylbenziminazoles [in characterisation of carbohydrates].—See A., 1941, II, 53.

Isomerisation of hydroxyaldehydes. VII. Re-grouping of galactose, and galactodesonic acid. VIII. Conversion of *l*-arabinose into *l*-arabosaccharic acid. A. M. Gachokidze (*J. Gen. Chem. Russ.*, 1940, **10**, 497—506, 507—512).—VII. Galactal triacetate (**I**) and Cl_2 or Br in $CHCl_3$ yield 1 : 2-*dichloro*-, m.p. 105°, $[\alpha]_D$ +188·7° (all $[\alpha]_D$ refer to $CHCl_3$ solutions), or 1 : 2-*dibromo-galactose triacetate*, decomp. at the b.p., $[\alpha]_D$ +17·8°. These react with moist Ag_2CO_3 in $CHCl_3$ to yield 2-*chloro*- (**II**), $[\alpha]_D$ +76·4°, or 2-*bromo-galactose triacetate*, uncrystallisable syrups. (**II**) when heated with aq. PbO (30 hr. at 100°) yields *galactodesonic acid* (**III**), m.p. 155—158°, $[\alpha]_D$ +6·8° [*Ba* and *Ca* salts; *lactone*; *phenylhydrazide*, m.p. 170—173°; *tetra-acetate*, m.p. 125—128° (*phenylhydrazide*, m.p. 150°)]. With MeI and Ag_2O (40 hr. at 35—40°) (**III**) yields *Me tetramethylgalactodesonate*, m.p. 83—85°, $[\alpha]_D$ +69·8°. Galactal is methylated similarly to 3 : 4 : 6-*trimethylgalactal*, a syrup, $[\alpha]_D$ −35·45°, from which the following substances are prepared [as from (**I**)]: 1 : 2-*dichloro*-, $[\alpha]_D$ +110·2°, and 2-*chloro*-3 : 4 : 6-*trimethylgalactose*, and 3 : 4 : 6-*trimethylgalactodesonic acid* (*Ba* salt; *phenylhydrazide*, m.p. 130—135°).

VIII. *l*-Arabinal diacetate in $CHCl_3$ and Cl_2 afford 1 : 2-*dichloro*-l-*arabinose diacetate*, m.p. 100—101°, $[\alpha]_D$ +166°, which with moist Ag_2CO_3 gives 2-*chloro*-l-*arabinose diacetate*, a syrup, $[\alpha]_D$ +150·5°. This when heated with PbO in H_2O (120 hr. at 100°) yields *l*-arabodesonic acid (*Ba* salt; *lactone*, m.p. 155°; *phenylhydrazide*, m.p. 175—180°), from which *Me trimethyl*-l-*arabodesonate*, m.p. 102—105°, is obtained by the action of Me_2SO_4. R. T.

Determination of the relationship between refractive index and specific rotation in mixtures of 2 : 3 : 4 : 6-tetramethyl-α- and -β-methyl-*d*-galaotosides. D. J. Bell (*J.C.S.*, 1940, 1543—1545).—The graphical relationship between *n* and $[\alpha]$ of mixtures of α- and β-forms of 2 : 3 : 4 : 6-tetramethylmethyl-*d*-galactoside has been found to be a straight line.

F. R. S.

Carbohydrate sulphuric esters. I. Glucose and galactose sulphates. E. G. V. Percival and T. H. Soutar (*J.C.S.*, 1940, 1475—1479).—Galactose in C_5H_5N with $ClSO_3H$ in $CHCl_3$ at −10°, followed by PbO and $BaCO_3$, yields a crude salt from which *brucine galactose sulphate*, $[\alpha]_D^{17}$ −5° (5 min. in H_2O), −11° (24 hr.), and the *Ba* salt (**I**), $[\alpha]_D^{18}$ +46° in H_2O, are obtained. Di*iso*propylidenegalactose similarly yields *Ba* di*iso*propylidenegalactose 6-*sulphate* (**II**), $[\alpha]_D^{14}$ −35·7° in H_2O, and, by hydrolysis (1% AcOH), *brucine*, $[\alpha]_D^{18}$ +5° (30 min. in H_2O), +1° (24 hr.) [*dihydrate*, $[\alpha]_D^{18}$ +5° (30 min. in H_2O), +1° (24 hr.)], and *Ba galactose* 6-*sulphate* [different from (**I**)], $[\alpha]_D^{18}$ +56° in H_2O, converted into (**I**) by $COMe_2$ and a trace of H_2SO_4, followed by $BaCO_3$. Ba α-methylglucoside and *galactoside sulphate*, $[\alpha]_D^{17}$ +142° in H_2O (from α-methylgalactoside as above), with aq. $Ba(OH)_2$ at 100° yields *anhydromethylhexosides*, m.p. 105—106°, $[\alpha]_D^{15}$ +52° and +50·2° in H_2O respectively. The rates of hydrolysis of these Ba salts and Ba glucose sulphate (**III**) by 0·1N-HCl have been determined, but are not suitable for distinguishing the salts. At 100°, (**I**) and (**III**) are immediately hydrolysed, with decomp., by 0·1N-NaOH, whilst (**II**) is unaffected by 2N-NaOH.

A. Li.

Fructosephenylmethylhydrazone. W. J. Heddle and E. G. V. Percival (*J.C.S.*, 1940, 1511—1512; cf. A., 1937, II, 400).—Ofner's prep. of fructosephenylmethylhydrazone (A., 1905, i, 937) has been repeated, giving a product, m.p. 118—119°, $[\alpha]_D^{18}$ ±0° in C_5H_5N–EtOH (4 : 6), which on acetylation gave only a syrup, $[\alpha]_D^{17}$ −75° in $CHCl_3$. A. Li.

Action of sulphuric acid of a certain concentration on sucrose. M. Fukui (*J. Chem. Soc. Japan*, 1936, **57**, 424).—A condensation product of sucrose (**I**) is obtained as a hydrophilic colloid containing no SO_4 by the action of 75% H_2SO_4 on (**I**) at 0—5°. Ch. Abs. (*e*)

Cellobiosazone, galactosazone, and other sugar osazones. J. R. Muir and E. G. V. Percival (*J.C.S.*, 1940, 1479—1481; cf. A., 1937, II, 400).—*Cellobiosazone hepta-acetate* (Ac_2O in C_5H_5N), m.p. 90°, $[\alpha]_D^{18}$ −37° in $CHCl_3$, on hydrolysis (H_2O–$COMe_2$–NaOH) yields *anhydrocellobiosazone hydrate* (**I**), m.p. 218°, $[\alpha]_D^{18}$ −142° in MeOH, identical with that obtained by Diels' method (A., 1936, 1364). Acetylation of (**I**) yields a *penta-acetate*, m.p. 193°, $[\alpha]_D^{18}$ −142° in $COMe_2$, deacetylated to (**I**). No cryst. deacetylation products could be obtained from the *hepta-acetates* of *melibiosazone*, m.p. 105°, $[\alpha]_D^{17}$ +32° in $CHCl_3$, or *gentiobiosazone*, m.p. 98°, $[\alpha]_D^{17}$ −46° in $CHCl_3$. Methylation (Me_2SO_4) of galactosazone (**II**) yields *trimethylgalactose methylphenylphenylosazone* (**III**), m.p. 160°, $[\alpha]_D^{18}$ +86·5° (5 min. in $CHCl_3$), +32·4° (48 hr.). (**II**) does not react with CPh_3Cl in C_5H_5N. It is concluded that (**II**) contains a tagatopyranose ring. (**II**) with *p*-NO_2·C_6H_4·CHO gives a 30% yield of galactosone, but no osone could be so obtained from (**III**). A. Li.

Seed mucilages. I. Mucilaginous polysaccharide of the seed of *Plantago lanceolata*. J. Mullan, E. G. V. Percival, and [in part] R. Burnett (*J.C.S.*, 1940, 1501—1506).—Pptn. of the aq. extract of the seeds with EtOH yields an acid polysaccharide (**I**), $[\alpha]_D^{16}$ −60° in H_2O, equiv. wt. 1100, uronic anhydride 15·2%, pentosan 72%, and methylpentosan 11%. Hydrolysis ($H_2C_2O_4$) of (**I**) and treatment with $CaCO_3$ gives *a-d*-xylose and (30%) the Ca salt, $(C_{12}H_{21}O_{11})_2Ca$, $[\alpha]_D^{17}$ +89° in H_2O, of an aldobionic acid having a methylpentosan residue. Hydrolysis (15% H_2SO_4) of (**I**) gives an acid (? galacturonic) (Ba salt, $[\alpha]_D^{16}$ +22° in H_2O) which suffers a reversal of rotation in presence of 1% MeOH–HCl, and is oxidised (aq. Br or HNO_3) to mucic acid. Acetylation (Ac_2O in C_5H_5N) of (**I**) yields fractions (*A*) (40%), Ac 41·0%, $[\alpha]_D^{17}$ −72° in $COMe_2$ (methylated product, OMe 35%, $[\alpha]_D^{18}$ −104° in $CHCl_3$), and (*B*), Ac 36%, unaffected by further acetylation, methylated to a product, OMe 34%, $[\alpha]_D^{18}$ −99° in $CHCl_3$, having a mol. size (η in *m*-cresol) double the corresponding val. for (*A*). Methylation of acetylated (**I**), hydrolysis (MeOH–HCl), and fractionation yields trimethylmethylxylopyranosides (30%), 3 : 4-dimethylmethylxylopyranosides (**II**) (28%), a mixture of (**II**) with 2 : 4 : 6-trimethylmethylgalactosides (**III**) (isolated as the tri- and tetra-methylgalactose anilides) and glycosides of lower OMe content (22%), and a mixture of (**III**) with a partly methylated methyluronoside (Ba salt of hydrolysis product, OMe 17·7%, $[\alpha]_D^{18}$ +43° in H_2O) and other glycosides (17%). Methylation and hydrolysis (2% HNO_3) of (**II**) yields trimethylxylopyranose. Hydrolysis of (**II**) gives dimethylxylose (**IV**), oxidised (aq. Br) to 3 : 4-*dimethylxylonolactone*, m.p. 67°, $[\alpha]_D^{18}$ +41° (5 min. in H_2O), +31° (4 hr., const. val.), converted by MeOH–NH_3 into the *amide*, $[\alpha]_D^{14}$ +54° in H_2O, which with NaOCl followed by NH_2·NH·CO·NH_2 gives a hydrazodicarbonamide, m.p. 257° (decomp.). Oxidation (HNO_3) and esterification of (**II**) yields *Me dimethoxyglutarate*, b.p. 130—150° (bath temp.)/0·05 mm., $[\alpha]_D^{16}$ +41° in MeOH [the amide from which gives a hydrazodicarbonamide, m.p. 254° (decomp.)], methylated (MeI–Ag_2O) to Me *i*-xylotrimethoxyglutarate. More vigorous oxidation (HNO_3) of (**II**), esterification, and amide formation gives some *l*-dimethoxysuccinamide. (**IV**) gives no cryst. anilide. A. Li.

Fractionation of potato starch by electrophoresis. R. H. Hopkins, E. G. Stopher, and D. E. Dolby (*J. Inst. Brew.*, 1940, **46**, 426—432).—Electrophoresis of starch, alternating with redispersion (*e.g.*, at 120°) of the amylopectin fraction, yields up to 80% of amyloamylose (**I**), which is more completely though less rapidly degraded by barley diastase than is the original starch. On keeping, (**I**) reverts to a form more closely resembling starch in its susceptibility to attack by this enzyme. I. A. P.

Theory of nitration of cellulose.—See A., 1941, I, 44.

Manufacture of aliphatic amines.—See B., 1940, 843.

Chemical war materials. XIX. Chemical and spectroscopic properties of ββ′β″-trichlorotriethylamine (skin poison) and its hydrochloride. H. Mohler and W. Hämmerle (*Helv. Chim. Acta*, 1940, **23**, 1211—1216).—$N([CH_2]_2$·$Cl)_3$,HCl (**I**), m.p. 131° (corr.), is detected by the formation of oily drops which become brown when warmed and the development of an odour of amines and geranium on addition of alkali to its solutions, by the production of a yellow turbidity in the cold and a brown ppt. on warming with Nessler's reagent (sensitiveness 1 in 5000), by the production of a picrate, m.p. 135° (corr.) (sensitiveness 1 in 1000), and by the formation of a picrolonate, m.p. 135° (corr.). The spectra of (**I**) in EtOH and of the base in hexane and EtOH resemble those of substances with a hetero-atom in the ring [furan, thiophen, pyrrole, yperite (**II**) and its derivatives]. It appears unlikely that (**I**) will replace (**II**) in warfare. H. W.

Complex sodium bismuth salts of triethanolamine and tri-*iso*propanolamine. W. T. Miller (*J. Amer. Chem. Soc.*, 1940, **62**, 2707—2709).—The prep. and properties of *Na bismuthyltriisopropanolamine*, *Na bismuthyltriethanolamine*, and *Bi triethanolamine* are given. These compounds represent new types of complex Bi salts. W. R. A.

Separation of amino-acids from acid hydrolysates of proteins.—See B., 1940, 843.

Resolution of synthetic alanine. E. Pascu and J. W. Mullen (*J. Biol. Chem.*, 1940, **136**, 335—342; cf. Fischer, A., 1899, i, 888).—Crystallisation of strychnine benzoyl-*dl*-alanine followed by removal of the alkaloid gives benzoyl-*l*(+)-alanine (73% yield); benzoyl-*d*(−)-alanine is obtained from the mother-liquors through the brucine salt. Hydrolysis (20% HCl) gives *l*(+)- and *d*(−)-alanine in 90% yields, without racemisation. Some racemisation occurs during benzoylation. A. Li.

Preparation of *dl*-asparagine and *dl*-aspartic acid. W. Cocker (*J.C.S.*, 1940, 1489—1491).—Reduction (Al–Hg) of CO_2Et·C(N·OH)·CH_2·CO_2Et yields Et_2 aspartate (*phenylcarbamido-*, m.p. 104°, and *Ac* derivative, b.p. 143—145°/4—5 mm.), which gives with H_2O at 140—150° under pressure, aspartic acid (*phenylhydantoin*, m.p. 225—225·5°; SO_2Ph derivative, m.p. 181—182°), and with aq. NH_3 at 100° under pressure, asparagine. A. Li.

Interaction of *n*-butyl alcohol and the chlorides and oxychlorides of phosphorus in absence and in presence of pyridine. W. Gerrard (*J.C.S.*, 1940, 1464—1469; cf. A., 1940, II, 127).—BuOH with PCl_3 at −10°, agitated by CO_2, yields PCl_2·OBu, *P di-n-butoxy chloride*, b.p. (impure) 90—110°/13 mm., and OH·$P(OBu)_2$, in proportions varying with the amounts of reagents and mode of addition. BuOH (3 mols.) with PCl_3 (1 mol.) and HCl gives BuCl, OH·$P(OBu)_2$, and (?) $(OH)_2P$·OBu. $P(OBu)_3$ with PCl_3 at room temp. gives PCl_2·OBu and $PCl(OBu)_2$. BuOH with $POCl_3$ at −5°, agitated by CO_2, yields n-*butoxyphosphoryl dichloride*, b.p. 90°/17 mm. $PO(OBu)_3$ with $POCl_3$ at 100° gives $POCl_2$·OBu or *di-n-butoxyphosphoryl chloride*, b.p. 132—133°/15 mm. (also obtained, with BuCl, from $P(OBu)_3$ and Cl_2 at −10°), according to proportions. $PO(OBu)_3$ with HCl gas at room temp. gives BuCl. PCl_3 and $POCl_3$ with BuOH and C_5H_5N in Et_2O at −10° give 90% yields of $P(OBu)_3$ and $PO(OBu)_3$ respectively. $POCl_2$·OBu with EtOH and C_5H_5N in Et_2O at −10° yields *Et$_2$ Bu phosphate*, b.p. 123°/15 mm. PCl_2·OBu with C_5H_5N or C_5H_5N,HCl at 100° yields $P(OBu)_3$, but no BuCl. $PCl(OBu)_2$ with C_5H_5N gives no BuCl. $POCl_2$·OBu with C_5H_5N at 0° or C_5H_5N,HCl at 100° yields BuCl and C_5H_5N–P compounds. $POCl(OBu)_2$ with C_5H_5N or C_5H_5N,HCl at 100° yields BuCl and a gum, C_5H_5N,$P_2O_4(OBu)_2$. With EtOH and C_5H_5N in Et_2O, $POCl(OBu)_2$ gives a mixture of $PO(OBu)_2$·OEt and $PO(OBu)(OEt)_2$, whilst $POCl_2$·OBu gives $PO(OBu)(OEt)_2$ and $PO(OEt)_3$. Thermal decomp. of PCl_2·OBu and $POCl_2$·OBu gives no BuCl. BuOH with PCl_5 and C_5H_5N in boiling Et_2O yields some BuCl and $PO(OBu)_3$. It is concluded that BuCl is produced by the action of HCl on Bu phosphorous or phosphoric esters (a reaction inhibited by C_5H_5N), not by decomp. of Bu chloro-phosphites or -phosphates. A. Li.

Silico-organic compounds. III. Preparation and reactions of silicon analogues of certain aliphatic orthoesters. H. W. Post and C. H. Hofrichter, jun. (*J. Org. Chem.*, 1940, **5**, 572—578; cf. A., 1938, II, 535).—The exchange of alkoxy-groups between the homologous alcohols and ethane- or propane-orthosiliconates takes place thus: $SiEt(OEt)_3 + ROH \rightleftharpoons SiEt(OEt)_2$·OR + EtOH. The co-ordination of alcoholic H results in the creation of a net positive charge on the Si atom of the mol. which can then exert an attractive force on the surrounding O atoms. The moving in of any particular O atom aids the elimination of the other alcohol and results in an exchange. The mechanism makes it possible for heavier compounds to form when the groups are larger. Thus, $2SiPr(OEt)_3 + BuOH \rightleftharpoons [(OEt)_2SiPr]_2O + Et_2O +$ BuOH. The formation of 1 : 3 compounds during alkoxy-

interchange between homologous alkyl orthosilicates has been established. Gradual addition of the product of the action of Mg–Cu and MeI in Et_2O to $Si(OEt)_4$ affords $SiMe(OEt)_3$, b.p. 150—151°/760 mm., *diethoxydimethylsilicane*, b.p. 110—111°/760 mm., and impure *Et methancsiliconate*, $Me{\cdot}SiO_2Et$, b.p. 73°/760 mm. $Si(OBu)_4$, b.p. 142—144°/3 mm., is prepared by dropwise addition of BuOH to $SiCl_4$. Dropwise addition of MgBuBr to $Si(OEt)_4$ affords *Et butaneorthosiliconate*, b.p. 190—193°/740 mm., in 27% yield whereas *tetrabutylsilicane*, b.p. 231°/760 mm., is derived by the addition of $Si(OEt)_4$ (0·825 mol.) to MgBuBr (4 mols.). *Et_3 Bu orthosilicate*, b.p. 82·5°/15 mm., and *Et_2 Bu_2 orthosilicate*, b.p. 100°/15 mm., are obtained in 22% and 30·4% yield by protracted boiling of a mixture of $Si(OEt)_4$ and $Si(OBu)_4$. An attempt to prepare Bu propaneorthosiliconate from $SiPr(OEt)_3$ and BuOH was unsuccessful. H. W.

II.—HOMOCYCLIC.

Introduction of an ethylenic linking into the trimethylene cycle. I. Attempted preparation of methylene*cyclo*propane by the action of zinc dust on γ-chloro-β-chloromethylpropene in alcoholic solution. II. Action of phosphorus pentachloride on acetyl*cyclo*propane. I. A. Djakonov (*J. Gen. Chem. Russ.*, 1940, **10**, 402—413, 414—426).—I. $OH{\cdot}CMe(CH_2Cl)_2$ does not eliminate H_2O when heated with **I**, o-$C_6H_4(CO)_2O$, $H_2C_2O_4$, Ac_2O, $KHSO_4$, $NaHSO_4$, or $MgSO_4$ (230—300°). With P_2O_5 at 110° the product is *αγ-dichloro-β-methylpropene* (**I**), b.p. 131—132°. An inseparable mixture of (**I**) with $CH_2{:}C(CH_2Cl)_2$ (**II**) is obtained by chlorination of $CH_2{:}CMe_2$, and this mixture when heated at 70—75° with Zn dust in 75% EtOH, in the hope of obtaining methylene-*cyclo*propene from (**II**), gives only $CH_2{:}CMe_2$.

II. *cyclo*Propyl Me ketone and PCl_5 at >20° yield *βε-dichloro-Δ^β-pentene*, b.p. 40—41°/8 mm., but not the expected α-chloroethenyl*cyclo*propane. The trimethylene ring cannot exist in conjugation with a double linking, and partakes of the nature of an unsaturated group. R. T.

Chlorination of benzene.—See B., 1940, 844.

Synthesis and properties of mono-*n*-alkylbenzenes. II. Preparation and properties of the intermediate ketones and hydrocarbons. T. Y. Ju, G. Shen, and C. E. Wood (*J. Inst. Petroleum*, 1940, **26**, 514—531; cf. A., 1940, II, 369).—C_6H_6–RCOCl (R = $[CH_2]_x$·Me) (Friedel–Crafts) in CS_2 afford COPhR (**I**), reduced (Clemmensen or better by H_2–Pd–C in EtOH) to CH_2PhR. Yields of (**I**) decrease as the val. of x increases from 4 to 13. Optimum conditions for reactions are discussed. Many physical consts. are recorded. Effects of increase in the val. of x on physical properties are discussed; the Ph group has the main influence even when x is large. Ph *n*-butyl, m.p. −9°, b.p. 116°/10 mm. (oxime, new m.p. 55°; 2 : 4-*dinitrophenylhydrazone*, m.p. 163·5°), *n*-amyl, b.p. 111·5°/4 mm. (*oxime*, m.p. 52·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 166°), *n*-hexyl, b.p. 141°/9 mm. (2 : 4-dinitrophenylhydrazone, new m.p. 135°), *n*-octyl, new m.p. 14°, b.p. 166°/9 mm. (semicarbazone, new m.p. 133·5°; *oxime*, m.p. 53·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 119·5°), *n*-undecyl, new m.p. 44—45°, b.p. 193—194°/9 mm. (*semicarbazone*, m.p. 98°; *oxime*, m.p. 64·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 101—102°), and *n*-tridecyl ketone, new m.p. 52—53°, b.p. 194—196°/4 mm. (semicarbazone, new m.p. 101°; *oxime*, m.p. 69·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 98—98·5°), afford *n*-amyl-, b.p. 204—205°/760 mm., *n*-hexyl-, b.p. 226—227°/760 mm., *n*-heptyl-, b.p. 240—241°/760 mm., *n*-nonyl-, b.p. 280—281°/760 mm., *n*-dodecyl-, new m.p. −3°, b.p. 172—173°/9 mm., and *n*-tetradecyl-benzene, m.p. 8·6°, b.p. 195—196°/9 mm., respectively. With the ketones, change in val. of d_4^{20} and η is linear with respect to temp.; increase in x decreases the val. of d and n. In the case of the hydrocarbons, increase in x decreases density for temp. <50°; at 70°, they have a similar density. Increase in x causes a decrease in n and an increase in η. A. T. P.

Isomerisation of unsaturated hydrocarbons in presence of oxides of metals. IV. Isomerisation of *p*-diallylbenzene and 1-allylnaphthalene in presence of aluminium oxide. R. J. Levina, L. E. Karelova, and I. A. Eliaschberg (*J. Gen. Chem. Russ.*, 1940, **10**, 913—916).—p-$C_6H_4(CH_2{\cdot}CH{:}CH_2)_2$ yields a mixture of $CH_2{:}CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH{:}CHMe$ and p-$C_6H_4(CH{:}CHMe)_2$ when passed over Al_2O_3 at 300°. 1-$C_{10}H_7{\cdot}CH_2{\cdot}CH{:}CH_2$ [*dibromide*, b.p. 212—213°/10 mm. (decomp.)], similarly yields 1-$C_{10}H_7{\cdot}CH{:}CHMe$. R. T.

Complex formation between polynitro-compounds and aromatic hydrocarbons and bases. IX. Influence of solvents on the temperature coefficients of colour densities. D. L. Hammick and (Miss) R. B. M. Yule (*J.C.S.*, 1940, 1539—1542).—The effect of temp. change in various solvents has been studied for the following colour-producing interactions: $C(NO_2)_4$ with $C_{10}H_8$ and 1- or 2-$C_{10}H_7Me$; $NHPh_2$ with o-$C_6H_4Cl{\cdot}NO_2$ and 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$. In *n*-C_6H_{14}, CCl_4, $C_2H_4Cl_2$, and $C_2H_2Cl_4$, the colour-producing interactions are exothermic, colour density decreasing with rise in temp. In COPhMe, *cyclo*hexanone, $COMe_2$ Pr^{α}OH, EtOH, and MeOH, the $C(NO_2)_4$ interactions are endothermic, colour increasing with rise of temp. No endothermic reactions have been observed in the polar chloronitrobenzene–$NHPr_2$ systems. The facts are discussed in the light of the work of Gibson and Loeffler (A., 1940, I, 344). F. R. S.

Production of styrene and related compounds. Simultaneous production of vinylaromatic compounds and arylacetylenes.—See B., 1940, 844.

Addition of bromine and chlorine to βγ-diphenylbutadiene. J. S. Salkind and P. Mosunov (*J. Gen. Chem. Russ.*, 1940, **10**, 517—520).—$(CH_2{:}CPh)_2$ and Br or Cl_2 in CCl_4 at 0° yield *αδ-dibromo-* or *αδ-dichloro-βγ-diphenylbutane*, m.p. 143—144°. R. T.

Orientation of chrysene. M. S. Newman and J. A. Cathcart (*J. Org. Chem.*, 1940, **5**, 618—622).—The sole product of the action of HNO_3 (*d* 1·42) and conc. H_2SO_4 on chrysene (**I**) suspended in glacial AcOH is 8-nitrochrysene (**II**), m.p. 214·0—214·6°, oxidised by CrO_3 or $Na_2Cr_2O_7$ in glacial AcOH to 8-nitrochrysenequinone, which could not be obtained pure and is characterised by condensation with o-$C_6H_4(NH_2)_2$ to *7-nitrochrysophenazine*, m.p. 277·6—279·6°. Under more drastic conditions of nitration (**I**) gives 2 : 8-*dinitrochrysene*, m.p. 380·5—382·5°. The structure of (**II**) is established by its reduction [red P and HI (*d* 1·5) in boiling AcOH] to 8-*aminochrysene* (**III**), m.p. 210·0—211·0°, converted by 10% H_2SO_4 at 220—225° into 8-chrysenol, m.p. 248—250° (acetate, m.p. 158·6—159·2°; Me ether, m.p. 127·2—127·8°). (**III**) dissolved in EtOAc and AcOH is transformed by short treatment with boiling Ac_2O containing fused NaOAc into 8-*acetamido-*, m.p. 299·5—301·0°, and by more protracted treatment with boiling Ac_2O into 8-*diacetylamino-*, m.p. 221·8—223·0° after softening at 218°, *-chrysene*. Dropwise addition of $ClSO_3H$ to a well-stirred suspension of I in *s*-$C_2H_2Cl_4$ affords *chrysene-8-sulphonic acid*, m.p. 193—194° when heated at the rate of 4° per min. [*Na* and p-$C_6H_4Me{\cdot}NH_2$ salt, m.p. 273—274·5° (decomp.) when heated at rate of 5° per min.], oriented by fusion with KOH at 220° and acetylation of the product to 8-chrysenyl acetate, m.p. 158·0—158·6°. H. W.

Catalytic reduction of *p*-chloromitrobenzene. A. Balandin and A. Titova (*Utschen. Zapiski*, 1934, **2**, 229—231).—In the hydrogenation of p-$C_6H_4Cl{\cdot}NO_2$ using Ni at 238°, p-$C_6H_4Cl{\cdot}NH_2$ was first formed, and no $PhNO_2$. Ch. Abs. (*e*)

Catalytic action of Japanese acid clays on mixtures of aniline and methyl alcohol vapours. K. Kobayashi and M. Mizushina (*Mem. Fac. Sci. Eng. Waseda Univ.*, 1937, No. 12, 50—51; *Chem. Zentr.*, 1938, ii, 3527).—The yields of p-$C_6H_4Me{\cdot}NH_2$ and NHPhMe (max. 85% at 400° and 28·2% at 250°, respectively) obtained by passing the vapours over the clay at 220—400° have been determined. The catalytic action of the clay is attributed to strong adsorption of the NH_2-group, which facilitates reaction between the *p*-H and the OH. A. J. E. W.

Hydration of substituted amides of stearic acid. B. A. Toms (*Nature*, 1940, **146**, 560; cf. A., 1940, I, 410; II, 125).—Percentages of bound H_2O in stearanilide and 15 derivatives are tabulated. Substitution in the nucleus has little effect on H_2O-binding capacity, but an o- or p-CO_2H reduces the amount of H_2O bound. Replacement of the H of the NHAr prevents hydration. An explanation of these effects is advanced. L. S. T.

Alleged reduction of the phenylurethane of trichlorolactic ester and nitrile by dilute aqueous alkali. H. Irving and H. Marston (*J.C.S.*, 1940, 1512—1513).—The compounds formed from $NHPh{\cdot}CO_2{\cdot}CHR{\cdot}CCl_3$ (**I**) (R = CN or CO_2Et) and 10% aq. NaOH, formulated as $NHPh{\cdot}CO{\cdot}O{\cdot}CHR{\cdot}CHCl_2$ by

Lambling (cf. A., 1899, i, 52), are now shown to be *ββ-dichloro-α-cyano-* or *-α-carbethoxy-vinyl phenylcarbamates*, $NHPh{\cdot}CO_2{\cdot}CR{:}CCl_2$ (**II**). (**I**) (R = CN) undergoes quant. elimination of HCl with cold Et_2O–NEt_3 to give (**II**) (R = CN). (**I**) (R = CN) and boiling aq. Na_2CO_3 yield $CHCl_2{\cdot}CO{\cdot}NHPh$ (mechanism of formation given) and $CCl_2{:}C<^{O-CO}_{CO\cdot NPh}$ [not $CHCl_2{\cdot}CH<^{O-CO}_{CO\cdot NPh}$ as formulated by Lambling], formed by independent reactions. A. T. P.

Preparation of derivatives of sulphanilamide. W. Cocker (*J.C.S.*, 1940, 1574—1576).—*p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and $CN{\cdot}CH_2{\cdot}NH_2,H_2SO_4$ with aq. NaOH afford N^4-*acetylsulphanilamido-acetonitrile* (**I**), m.p. 194—195°, and thence (H_2SO_4 at 45—85°) the *-acetamide*, m.p. 224—225°. Hydrolysis of (**I**) with conc. HCl at 100° (bath), evaporation to dryness, and extraction with EtOH gives the *hydrochloride*, m.p. 175°, of *Et sulphanilamidoacetate*, m.p. 92° (*Ac* derivative, m.p. 128°), similarly converted (conc. HCl; evaporation; MeOH) into the *Me* ester, m.p. 88·5—89°. (**I**) and MeOH–NaOMe–MeI or EtOH–NaOEt–EtI give N^4-*acetyl*-N^1-*methyl*- (**II**), m.p. 158—159°, or -N^1-*ethyl-sulphanilamido-acetonitrile* (**III**), m.p. 128—128·5°, and thence (H_2SO_4) the corresponding *-acetamides*, m.p. 185—186°, or 167—168°, respectively. (**II**) or (**III**) affords *Et* N^1-*methyl*-, m.p. 115° (corresponding *Me* ester, m.p. 105—106°), or *Et* N^1-*ethyl-sulphanilamidoacetate*, m.p. 88—89° (*Me* ester, m.p. 85), respectively. The substances have little therapeutic val. A. T. P.

Phosphoric acid derivatives of sulphanilamides.—See B., 1941, III, 21.

Naphthalene series. IX. Rearrangement of 1-naphthylamine-4-sulphonates to 1-naphthylamine-2-sulphonates. N. N. Voroshcov, V. V. Kozlov, B. V. Aristov, A. I. Barischev, and M. F. Fedulov (*J. Gen. Chem. Russ.*, 1940, **10**, 894—906).—Conversion of 1 : 4- (**I**) into 1 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3M$ (**II**) (M = Na, K, NH_4, 0·5Mg, 0·5Ba) involves the intermediate formation of 1-$C_{10}H_7{\cdot}NH{\cdot}SO_3M$ (**III**), isolated in small amount from the reaction product. The velocity of the reaction (**III**) → (**II**) is considerably > that of (**I**) → (**III**). R. T.

Reduction of aromatic nitro-compounds by hydrogen and Raney nickel at atmospheric temperature and pressure. A. Albert and B. Ritchie (*J. Proc. Roy. Soc. New South Wales*, 1940, **74**, 74—81).—H_2 and Raney Ni in EtOH during ¼—4 hr. reduce *m*-$C_6H_4(NO_2)_2$ to *m*-$C_6H_4(NH_2)_2$ (88% yield), 1 : 2 : 6-$C_6H_3Me(NO_2)_2$ to 1 : 2 : 6-$C_6H_3Me(NH_2)_2$ (90), 1 : 2 : 4-$C_6H_3Me(NO_2)_2$, 4 : 1 : 2-$NO_2{\cdot}C_6H_3Mc{\cdot}NH_2$, and 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}CHO$ to 1 : 2 : 4-$C_6H_3Me(NH_2)_2$ (96, 93, and 75, respectively), 3 : 5 : 1-$(NO_2)_2C_6H_3{\cdot}CO_2H$ to 3 : 5 : 1-$(NH_2)_2C_6H_3{\cdot}CO_2H$ (91), *o*- and *m*-$NO_2{\cdot}C_6H_4{\cdot}OH$ to *o*- and *m*-$NH_2{\cdot}C_6H_4{\cdot}OH$ (98 and 81, respectively), *m*-$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CHO$ to *m*-$NH_2{\cdot}C_6H_4{\cdot}NH{\cdot}CHO$ (93), (*m*-$NO_2{\cdot}C_6H_4)_2N{\cdot}CHO$ to (*m*-$NH_2{\cdot}C_6H_4)_2N{\cdot}CHO$ (92), 5 : 5′-dinitro- to 5 : 5′-diamino-diphenylamine-2-carboxylic acid (77), m.p. 71° (decomp.), and 5-nitro- to *5-amino-diphenylamine-2-carboxylic acid* (90), m.p. 140°. The amounts of H_2 absorbed show that the method might be suitable for determining NO_2-groups in a substance known not to contain other easily reducible systems. Reduction follows the normal course since a good yield of benzaldoxime *N*-Ph ether is obtained by partial reduction of $PhNO_2$ in presence of PhCHO. Preliminary results with compounds of the acridine series are summarised. A. Lt.

Manufacture of benzidine.—See B., 1941, II, 5.

Reductive ammonolysis of anthraquinone. N. N. Voroshcov and V. P. Schkitin (*J. Gen. Chem. Russ.*, 1940, **10**, 883—893).—Anthraquinone does not react with aq. NH_3 in presence or absence of $CuSO_4$ or $KClO_3$ at 200—220°. In presence of $(NH_4)_2SO_3$ and $Na_2S_2O_4$ the chief product is 9 : 10-*diaminoanthracene* (**I**), m.p. 142° (decomp.) [NN′-*Ac*$_2$, NN′-*Bz*$_2$, NN′-*dichlorocarbonyl*, m.p. 280° (decomp.), and NN′-*dibenzylidene*-derivative, m.p. 255°]. Air passed through a C_6H_6 solution of (**I**) (45 min. at 60°) yields 9 : 9′-*diamino*-10 : 10′-*dianthrylamine*, m.p. 141—142°, and 9 : 10-*dihydroxylaminoanthracene*, m.p. 155—156°. R. T.

New chemical reaction with the nitroxyl radical NOH. O. Baudisch (*Science*, 1940, **92**, 336—337; cf. A., 1940, II, 41). Freshly-prepared CuOH (0·5 g.) suspended in H_2O (200 c.c.) containing KNO_2 (0·5 g.), stirred with C_6H_6, dil. HCl (to p_H 2·5), and Merck's "superoxol" (**I**) (1 c.c.) yields Cu″ *o*-nitrosophenoxide (**II**). $Cu(NO_3)_2$ (1 g.) and KNO_2 (0·5 g.) in H_2O (200 c.c.), C_6H_6, (**I**) (1 c.c.), and *iso*ascorbic acid (or vitamin-*C*) (0·5 g.) also yield (**II**). Freshly-prepared CuOH (0·5 g.) suspended in H_2O (200 c.c.) containing benzenesulphohydroxamic acid (**III**) (0·5 g.), stirred (1 hr.) with C_6H_6, dil. HCl (to p_H 2·9), and (**I**) (1 c.c.) gives (after acidification) *o*-$NO{\cdot}C_6H_4{\cdot}OH$ and the H_2O-sol. Cu *o*-nitrosophenolsulphinate. CuOH (0·5 g.) in H_2O (200 c.c.) containing (**III**) (0·5 g.), HCl (to p_H 2·9), (**I**) (1 c.c.) on acidification (HCl) and extraction with Et_2O gives *o*-nitrosophenolsulphinic acid, which gives characteristically coloured Cu^{II}, Fe^{II}, Co, Ni, and Hg salts. These reactions are discussed. L. S. T.

2 : 4-Dinitro-6-*cyclo*hexylphenol.—See B., 1941, II, 6.

Condensation of $SiCl_4$ with dihydric phenols. J. N. Volnov and B. N. Dolgov (*J. Gen. Chem. Russ.*, 1940, **10**, 550—556). —*o*-$C_6H_4(OH)_2$ and $SiCl_4$ in light petroleum–Et_2O yield the *substance*, *o*-$C_6H_4<^{O}_{O}>SiCl_2$, in a polymerised form, probably of the type $[o\text{-}C_6H_4(O{\cdot})SiCl_2{\cdot}]_n$. This with EtOH gives *o*-$C_6H_4(OH)_2$, $Si(OEt)_4$, and HCl. *m*- and *p*-$C_6H_4(OH)_2$ similarly afford the *substances*, *m*-, b.p. 261°, and *p*-$C_6H_4(O{\cdot}SiCl_3)_2$, b.p. 267°, which with MeOH yield the respective *esters*, *m*- and *p*-$C_6H_4[O{\cdot}Si(OMe)_3]_2$. R. T.

Conversion of eugenol and its ethers into the corresponding propenyl compounds. T. F. West (*J.C.S.I.*, 1940, **59**, 275—276).—K eugenoxide (**I**) dissolved in a mixture of diethylene glycol and $N(CH_2{\cdot}CH_2{\cdot}OH)_3$ (**II**) is isomerised endothermally at ~160° to K *iso*eugenoxide. Eugenol Et ether heated at 190° with KOH in diethylene glycol Et_1 ether and (**II**) is converted into a mixture of *trans-* (70%) and *cis-iso*eugenol Et ether. With the appropriate RBr in hot H_2O, (**I**) gives eugenol Pr^{α}, b.p. 122—124°/2 mm., Pr^{β}, b.p. 114—115°/1 mm., and n-*amyl*, b.p. 150—153°/1 mm., *ether*. T. F. W.

Substituted indenes. I. V. M. Trikojus and D. E. White (*J. Proc. Roy. Soc. New South Wales*, 1940, **74**, 82—87).—5(or 6)-Methoxyindene (Ingold *et al.*, *J.C.S.*, 1923, **123**, 1469) with Br in CS_2 yields (cf. *loc. cit.*) a *dibromide*, m.p. 65—66°, decomp. >120° (blue liquid), a light petroleum solution of which with H_2O at 0° yields the *bromohydrin*, $C_{10}H_{11}O_2Br$, m.p. 117°. 4 : 5-*Dimethoxy*-1-*hydrindoneoxime*, m.p. 168°, is reduced (Na–Hg in hot 66% AcOH) to 4 : 5-dimethoxy-1-hydrindamine (*Ac* derivative, m.p. 176°), the *hydrochloride*, decomp. 209—210°, of which at 215—225°/22 mm. gives 4 : 5(or 6 : 7)-*dimethoxyindene*, m.p. 32°. The following were prepared by similar methods: 5 : 6-*dimethoxy*-1-*hydrindoneoxime*, m.p. 196°, *-hydrindamine hydrochloride*, decomp. 249—250°, and (by heating at 270°/atm. pressure) *-indene*, m.p. 71°; 5 : 6-*methylenedioxy*-1-*hydrindamine hydrochloride*, decomp. 254—255°, and *-indene*, m.p. 87—88°; 5-*methoxy*-6-*ethoxy*-1-*hydrindone*, m.p. 138—139° (from 3 : 4 : 1-$OMe{\cdot}C_6H_3(OEt){\cdot}[CH_2]_2{\cdot}CO_2H$ and P_2O_5 in boiling C_6H_6) (*oxime*, m.p. 188—189°), and *-hydrindamine hydrochloride*, m.p. 268—270° (decomp.), and 5(or 6)-*methoxy*-6(or 5)-*ethoxyindene*, m.p. 65—66°. A. Lt.

Nitro-derivatives of diphenyl ether-4-sulphonic acid. N. N. Voroschcov, jun. (*J. Gen. Chem. Russ.*, 1940, **10**, 935—941). —4-Sulphodiphenyl ether when nitrated yields 2 : 4′-*dinitro*- (**I**) (*Na* salt, $+3H_2O$; *Ba* salt; *chloride*, m.p. 134—136·5°) and 2 : 2′ : 4′-*trinitro*-4-*sulphodiphenyl ether* (**II**) (*Na* salt, $+H_2O$; *chloride*, m.p. 157—159°; *amide*, m.p. 188—190°), further nitration of which gives 2 : 4 : 2′ : 4′-tetranitrodiphenyl ether (**III**). (**I**) and boiling aq. NaOH afford 2 : 1 : 4-$NO_2{\cdot}C_6H_3(OH){\cdot}SO_3H$ (**IV**) and *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$. (**V**); (**II**) similarly yields (**IV**) and 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}OH$ (**VI**). Aq. NH_3 and (**I**) at 100° afford (**V**) and 2 : 1 : 4-$NO_2{\cdot}C_6H_3(NH_2){\cdot}SO_3H$ (**VII**); (**II**) gives 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NH_2$ (**VIII**) and (**IV**). The chloride of (**I**) with aq. NH_3 gives (**V**) and the amide of (**VII**); that of (**II**) gives (**VIII**) and the amide of (**IV**). (**III**) and aq. NH_3 or NH_2Ph afford (**VI**) and (**VIII**) or 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}NHPh$, respectively. R. T.

Synthesis of local anæsthetics. IV. K. N. Gaind, J. N. Ray, and J. N. Yajnik (*J. Indian Chem. Soc.*, 1940, **17**, 400—404).—*o*-$OEt{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2Cl$ and piperidine in boiling C_6H_6 give *piperidinoacet-o-phenetidide*, m.p. 98° (*hydrochloride*, m.p. 158°). Diethylaminoacet-, an oil (*hydrochloride*, m.p. 118°), *β-chloropropion-*, m.p. 77°, and *β*-piperidinopropion-, an oil (*hydrochloride*, m.p. 102°), *-o*-phenetidide are obtained analogously. The following are described. *Hydrochlorides* of *β-diethylaminopropion-o-phenetidide*, m.p.

126°, *piperidinoacet*-m-*phenetidide* (I), m.p. 159°, and *diethylaminoacet*-m-*phenetidide*, m.p. 180°. *β-Chloropropion*-m-*phenetidide*, m.p. 80—81°, and *β-piperidinopropion*-m-*phenetidide hydrochloride*, m.p. 244° (the β-diethylamino-derivative hydrochloride is an undistillable liquid); *piperidinoacet*-p-*phenetidide*, (II), m.p. 67°; *diethylaminoacet*-p-*phenetidide hydrochloride*, m.p. 154°; *β-chloropropion*-p-*phenetidide*, m.p. 123°; *β-piperidinopropion*-p-*phenetidide*, m.p. 96° (*hydrochloride*, m.p. 199°). *Hydrochlorides* of *β-diethylaminopropion*-p-*phenetidide*, m.p. 119°, *piperidinoacet*-o-*anisidide*, m.p. 104°, *diethylaminoacet*-o-*anisidide*, m.p. 171°, *β-piperidinopropion*-o-*anisidide*, m.p. 184°, *piperidinoacet*-m-*anisidide*, m.p. 154°, *diethylaminoacet*-m-*anisidide*, m.p. 144°, *β-piperidinopropion*-m-*anisidide*, m.p. 194°, *β-diethylaminopropion*-m-*anisidide*, m.p. 128°, *piperidinoacet*-p-*anisidide*, m.p. 160°, and *diethylaminoacet*-p-*anisidide*, m.p. 190°. *β-Diethylaminopropion*-o-*anisidide picrate*, m.p. 173°, *β-chloropropion*-m-*anisidide*, m.p. 92°, *β-chloropropion*-p-*anisidide*, m.p. 124°, *β-piperidinopropion*-p-*anisidide*, m.p. 104°, and *β-diethylaminopropion*-p-*anisidide picrate*, m.p. 123°. Substances in the *m*-series have pronounced local anæsthetic action reaching its max. in (I). In the *p*-phenetidine series appreciable activity is displayed by (II). In both compounds the side-chain has the piperidinoacetyl residue. H. W.

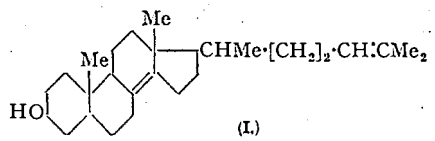
Reactions of 2 : 6-dichloro- and 2 : 4 : 6-trihalogeno-nitrobenzenes with a mercaptide reagent. J. D. Loudon (*J.C.S.*, 1940, 1525—1528).—Equimol. amounts of 2 : 6 : 1-$C_6H_3Cl_2{\cdot}NO_2$ (I) and *p*-$C_6H_4Me{\cdot}SH$ (II) in aq.-NaOH–EtOH at room temp. (3 weeks) afford unchanged (I), (*p*-$C_6H_4Me{\cdot}S)_2$, 2-*chloro*-6-p-*tolylthiol*-, m.p. 82—83° (H_2O_2–AcOH at 100° give the *sulphone*, m.p. 151°), and 2 : 6-*di*-p-*tolylthiol-nitrobenzene*, m.p. 168—169° (best prepared in EtOH) (*disulphone*, m.p. 196°). 2 : 4 : 6 : 1-$C_6H_2Cl_3{\cdot}NO_2$ (III) (1 mol.) [from *s*-$C_6H_3Cl_3$ and HNO_3 (*d* 1·5 + *d* 1·42) at 100°] and (II) (3 mols.) in NaOH–EtOH, heated for 10 min., afford 2 : 4 : 6-*tri*-p-*tolylthiol*- (IV), m.p. 142° [similarly obtained from (VI) (below)] [the *trisulphone*, m.p. 230°, and piperidine give 1-*piperidino*-2 : 4 : 6-*tri*-p-*toluenesulphonylbenzene*, m.p. 188°], and 4-*chloro*-2 : 6-*di*-p-*tolylthiol-nitrobenzene* (V), m.p. 206—207° (softens at 200°) (*disulphone*, m.p. 211°); (V) is best prepared from (III) (1 mol.) and (II) (2 mols.) in cold aq. EtOH–NaOH–dioxan, and with excess of piperidine yields 4-*piperidino*-2 : 6-*di*-p-*tolylthiolnitrobenzene*, m.p. 205°. Equimol. quantities of (III) and (II) in EtOH–NaOH afford (V) and 2 : 4-*dichloro*-6-p-*tolylthiolnitrobenzene*, m.p. 97° (*sulphone*, m.p. 171°). Similarly prepared from 2 : 4 : 6 : 1-$C_6H_2Br_3{\cdot}NO_2$ (VI) are 4-*bromo*-2 : 6-*di*-, m.p. 210°, and 2 : 4-*dibromo*-6-p-*tolylthiolnitrobenzene*, m.p. 132°, and 4-*bromo*-2 : 6-*di*-, m.p. 223°, and 2 : 4-*dibromo*-6-p-*toluenesulphonylnitrobenzene*, m.p. 182°. 4 : 3 : 5 : 1-$NO_2{\cdot}C_6H_2Cl_2{\cdot}NHAc$ and (II)–NaOH–EtOH (refluxed) yield 4-*nitro*-3 : 5-*di*-p-*tolylthiol-acetanilide*, m.p. 261°; the corresponding *-aniline*, m.p. 270° affords (V) by the diazo-reaction. Equimol. amounts of 2 : 3 : 5 : 1-$NO_2{\cdot}C_6H_2Cl_2{\cdot}NHAc$ and (II) in NaOH–EtOH at room temp. afford 5-*chloro*-2-*nitro*-3-p-*tolylthiol-acetanilide*, m.p. 166—167°, and thence the *-aniline*, m.p. 110—111°; in hot aq. EtOH 2 mols. of (II) give 2-*nitro*-3 : 5-*di*-p-*tolylthiol-acetanilide*, m.p. 188°, and thence the corresponding *-aniline*, m.p. 117°, which affords 2-*chloro*-4 : 6-*di*-p-*tolylthiolnitrobenzene*, m.p. 104° [*disulphone*, m.p. 174°; 2-*piperidino*-4 : 6-*di*-p-*tolylthiolnitrobenzene*, m.p. 135°; with (II) yields (IV)]. (I) or (VI), refluxed with excess of piperidine, gives 2-*chloro*-, m.p. 63°, or 2 : 4-*dibromo*-6-*piperidinonitrobenzene*, m.p. 167°, respectively. The corresponding derivative from (III) could not be crystallised. Theoretical considerations are discussed. (II) in piperidine–dioxan give a stable *piperidine* salt.

A. T. P.

Significance of oxidation of adrenaline to benzoquinone.—See A., 1940, III, 895.

Activation of cholesterol.—See B., 1941, III, 21.

Sterol group. XLII. Constitution of zymosterol. B. Heath-Brown, I. M. Heilbron, and E. R. H. Jones (*J.C.S.*, 1940, 1482—1489).—Zymosterol dibromide, m.p. 157°, $[\alpha]_D^{20}$ +7·4° (A., 1929, 1443), is converted by Zn dust–95% AcOH at room temp. or Zn dust (activated with NH_4Cl) in boiling EtOH into zymosterol (I), m.p. 107—109°, $[\alpha]_D^{20}$ +50° (acetate, m.p. 107—108°, $[\alpha]_D^{20}$ +35°), also obtained by fractional crystallisation of the benzoate and hydrolysis with 3% KOH–EtOH (method: Wieland *et al.*, A., 1929, 1200). (I) is a $\Delta^{8:14\text{-}14:25}$-cholestadienol and is the first example of a natural sterol devoid of the 5 : 6-ethenoid linking. With BzO_2H–$CHCl_3$ at 0° (I) absorbs 2·1 O per mol. in 24 hr.; no evidence



(I.)

of the formation of an αβ-unsaturated ketone is obtained on oxidation by the Oppenauer method (A., 1937, II, 250). Reduction (H_2, PtO_2, AcOH–Et_2O) at atm. pressure of (I) affords α-zymostenol (II), m.p. 119—120°, $[\alpha]_D^{20}$ +20·8° [acetate, m.p. 77—78°, $[\alpha]_D^{20}$ +7·6°; *benzoate* (III), m.p. 109—111°, $[\alpha]_D^{20}$ +6·4°], which absorbs 1·9 O per mol. in 24 hr., and is almost certainly identical with α-cholestenol; it is isomerised by dry HCl–$CHCl_3$ at 20° to an α- + β-zymostenol complex, m.p. 98—99°, $[\alpha]_D^{20}$ +26·9° (absorbs 1·1 O per mol. in 24 hr.) (acetate, m.p. 70—71°, $[\alpha]_D^{20}$ +11·0°). (III) and HCl–$CHCl_3$ at 0° give *β-zymostenyl benzoate*, m.p. 165—166°, $[\alpha]_D^{20}$ +31·9°, and thence (3% KOH–EtOH) *β-zymostenol* (IV), m.p. 128°, $[\alpha]_D^{20}$ +30·5° (*acetate*, m.p. 76—77°), probably identical with β-cholestenol (cf. acetate, m.p. 91—92°). Reduction (H_2, PtO_2, AcOH) of (IV) affords crude (V), which when treated with Ac_2O–CCl_4–H_2SO_4 followed by 3% KOH–EtOH gives pure zymostanol (V), m.p. 140—141°, $[\alpha]_D^{20}$ +24·8°, identical with cholestanol. Zymostanyl acetate, new m.p. 114—116°, $[\alpha]_D^{20}$ +10·9° (also obtained from β-zymostenyl acetate containing some α-isomeride by hydrogenation and treating the product with Ac_2O–H_2SO_4), *benzoate*, m.p. 131—133°, $[\alpha]_D^{20}$ +17·8°, and *phenylurethane*, m.p. 155—156°, $[\alpha]_D^{20}$ +11·3°, are identical with cholestanyl acetate, benzoate, and *phenylurethane*, m.p. 151° (mixed m.p. 151—153°), respectively. (V) and CrO_3–AcOH at 20° give *zymostanone* (VI), m.p. 125—126°, $[\alpha]_D^{20}$ +40°, identical with cholestanone, which with Br–AcOH + a little HBr–AcOH yields *bromozymostanone*, m.p. 166—167°, identical with 2-bromocholestanone, m.p. 167—168°. (V) and CrO_3–90% AcOH at 60° give *zymostane*-C_2||C_3-*dicarboxylic acid*, m.p. 196—197°, $[\alpha]_D^{20}$ +33·4° (*Me*$_2$ ester, m.p. 50°, $[\alpha]_D^{20}$ +23·7°), identical with the acid, m.p. 195—196° (Me_2 ester, m.p. 58—60°), prepared similarly from cholestanol. (VI) and Zn–Hg in AcOH–HCl afford *zymostane*, m.p. 74—76°, $[\alpha]_D^{20}$ +20·9°, identical with cholestane, m.p. 79—80°. Ozonolysis of (I) in AcOH gives a little CH_2O and 52% of $COMe_2$; (II) similarly affords no $COMe_2$. (II) and SeO_2 in aq. EtOH afford *dehydro-α-zymostenol*, m.p. 98—99°, $[\alpha]_D^{20}$ −9·1°, which gives no colour with $SbCl_3$–$CHCl_3$ [dehydro-α-ergostenol (VII) gives a faint pink colour]. It exhibits light absorption (max. at 2475 A.) similar to that of (VII). All [α] are in $CHCl_3$.

A. T. P.

Action of phosphorus halides and thionyl chloride on benzilic acid. S. A. Setlur and V. V. Nadkarny (*Proc. Indian Acad. Sci.*, 1940, **12**, **A**, 266—269).—PCl_5 appears first to attack the alcoholic OH of $OH{\cdot}CPh_2{\cdot}CO_2H$ (I) since in mol. proportions in C_6H_6 the reactants afford $POCl_3$ and $CPh_2Cl{\cdot}CO_2H$ (II), m.p. 120° (decomp.). With 5 mols. of PCl_5 followed by $(NH_4)_2CO_3$ (I) affords $OH{\cdot}CPh_2{\cdot}CO{\cdot}NH_2$, m.p. 153°, with intermediate formation of $CPh_2Cl{\cdot}COCl$. PCl_3 and (I) afford (II) (also obtained with $SOCl_2$ at room temp.). H. W.

Oxygen inhibition in photobromination of cinnamic acid.—See A., 1941, I, 54.

Resolution of *dl*-phenylalanine by asymmetric enzymic synthesis. O. K. Behrens, D. G. Doherty, and M. Bergmann (*J. Biol. Chem.*, 1940, **136**, 61—68).—In presence of cysteine–papain, *acetyl*-d-*phenylalanylglycine*, m.p. 159—161°, $[\alpha]_D^{26}$ −1·90° in MeOH, with NH_2Ph forms the *anilide*, m.p. 208—209°, $[\alpha]_D^{25}$ −21·0°; reaction is very much slower than with the *l*-form (cf. A., 1938, II, 364). Details are given for the prep. of *d*- and *l*-phenylalanine starting from acetyl-*dl*-phenylalanylglycine and NH_2Ph, with subsequent hydrolysis (aq. HCl) of the anilides. The following (prep. by standard methods) are described: *carbobenzyloxy*-l-*phenylalanylglycine*, m.p. 151—152°, $[\alpha]_D^{26}$ −9·6° in AcOH, and its *anilide*, m.p. 180°, $[\alpha]_D^{26}$ +9·3° in AcOH; *carbobenzyloxy*-d-*phenylalanylglycine*, m.p. 150—151°, $[\alpha]_D^{25}$ +9·7° in AcOH, its *Et* ester, m.p. 109—111°, and *anilide*, m.p. 179°, $[\alpha]_D^{27}$ −9·4° in AcOH; *acetyldehydrophenylalanyl*-l-*leucine*, m.p. 218—219° (decomp.), and its *anilide*, m.p. 205—206, $[\alpha]_D^{25}$ −5·6° in AcOH; *acetyl*-l-*phenylalanyl*-l-*leucine*, m.p. 191—193°, $[\alpha]_D^{29}$ −5·4° in abs.

EtOH, and its *anilide*, m.p. 234—235°, $[\alpha]_D^{25}$ −41·7° in AcOH; *acetyl*-d-*phenylalanyl*-l-*leucine*, m.p. 183—184°, $[\alpha]_D^{29}$ −8·3° in abs. EtOH, and its *anilide*, m.p. 205—206°, $[\alpha]_D^{25}$ −24·8° in AcOH; *acetyl*-d-*phenylalanyl*-l-*glutamic acid* (anhyd. and +0·5H_2O), m.p. ~115° (softens at 95°), decomp. >240°, $[\alpha]_D^{25}$ −9·1° in MeOH, its *Me*$_2$ ester, m.p. 129°, $[\alpha]_D^{25}$ −20·7° in MeOH, and monoanilide, new m.p. 232—233°, $[\alpha]_D^{24}$ −118·1° in C_5H_5N; *acetyldehydrophenylalanyl*-l-*proline* (+0·5H_2O), m.p. 140—142°; two stereoisomeric forms of *acetylphenylalanyl*-l-*proline* (+H_2O), m.p. 174—175°, or (+0·5EtOH) m.p. 142°, and 186—187°, $[\alpha]_D^{25}$ −35·3° and −72·7° in MeOH, respectively. The *l*-phenylalanyl compounds form the anilides more rapidly than the *d*, except the proline derivatives which do not form anilides under the conditions described.

E. M. W.

***dl*-Deuterophenylalanine (benzoyl derivative, m.p. 185—186·5°) and deuterophenylacetic acid, m.p. 76·5—77°.**—See A., 1940, III, 917.

Thermal decomposition of benzoyl peroxide.—See A., 1941, I, 54.

Acetylsalicyl azide, m.p. 56—58° (decomp.), and benzylurethane, m.p. 74—76°. Salicylglycine Et ester, m.p. 98—99°. Acetylsalicylglycine, m.p. 147—149°.—See A., 1941, III, 56.

Reactivity of ·CHCl·CCl$_3$ group attached to an aromatic nucleus. H. V. Dharwarkar and R. L. Alimchandani (*J. Indian Chem. Soc.*, 1940, **17**, 416—421).—CCl_3·CH(OH)$_2$ and *o*-OH·C_6H_4·CO_2H in conc. H_2SO_4 containing NaCl in a closed flask yield 2-*hydroxy*-5-*αβββ*-*tetrachloroethylbenzoic acid* (**I**), m.p. 182—183° (*Ac* derivative, m.p. 146—147°; *anilide*, m.p. 201—202°; p-*toluidide*, m.p. 178—179°), also obtained by saturating a solution of 5 : 2 : 1-CCl_3·CH(OH)·C_6H_3(OH)·CO_2H in conc. H_2SO_4 with dry HCl. (**I**) and aq. NH_3 in 96% EtOH at room temp. afford 2-*hydroxy*-5-*βββ*-*trichloro*-*α*-*aminoethylbenzoic acid*, m.p. 212° after charring at 183—184°; the *α*-*anilino*-*acid* has m.p. 182° (decomp.). Gradual addition of Zn dust to a hot solution of (**I**) in AcOH yields 2-*hydroxy*-5-*ββ*-*dichlorovinylbenzoic acid*, m.p. 170—171°, which does not absorb Br in AcOH or $CHCl_3$, decolorises $KMnO_4$, and gives a blue colour with $FeCl_3$; it is also obtained by use of KI in boiling $COMe_2$. KCN and (**I**) in boiling aq. EtOH give 2-*hydroxy*-5-*ββ*-*dichloro*-*α*-*cyanovinylbenzoic acid*, m.p. 224—225° (*Ac* derivative, m.p. 175—176°; *dibromide*, m.p. 210°), hydrolysed by KOH–EtOH to 4-*hydroxy*-3-*carboxyphenylacetic acid*, m.p. 207°, and oxidised (H_2O_2–5% NaOH) to 4 : 1 : 3-OH·C_6H_3(CO_2H)$_2$, m.p. 303°. 2-Methoxy-5-*αβββ*-tetrachloroethylbenzoic acid, m.p. 138° (*Me* ester, m.p. 105°), is converted by boiling 15% KOH–EtOH into 2-*methoxy*-5-*αββ*-*trichlorovinylbenzoic acid*, m.p. 151—152° [*Ca* salt (+5·5H_2O); *Me* ester, m.p. 85°], which does not absorb Br in AcOH, $CHCl_3$, or CCl_4 or decolorise cold $KMnO_4$. *p*-OH·C_6H_4·CO_2H and CCl_3·CH(OH)$_2$ afford 4-*hydroxy*-3-*αβββ*-*tetrachloroethylbenzoic acid*, m.p. 142° (decomp.) (*Ac* derivative, m.p. 189—190°), converted by KI in boiling 96% EtOH into 4-*hydroxy*-3-*ββ*-*dichlorovinylbenzoic acid*, m.p. 171°. 4-Methoxy-3-*αβββ*-tetrachloroethylbenzoic acid, m.p. 248—249° (*Me* ester, m.p. 110—111°), is converted by boiling 20% KOH–EtOH into 4-*methoxy*-3-*αββ*-*trichlorovinylbenzoic acid*, m.p. 212—213°. The inactivity of α-Cl of the OMe-derivatives is ascribed to OMe which causes a large diminution in the ionising tendency of α-Cl by a supply of electrons and as a result the halogen atom becomes resistant towards anionic attack by NH_3, NH_2Ph, KI, and KCN.

H. W.

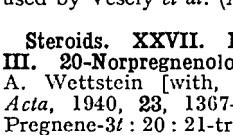
Mobility of groups in benzonitriles. C. W. N. Holmes and J. D. Loudon (*J.C.S.*, 1940, 1521—1525).—Careful addition of 10% aq. NaOH to 1 : 4 : 2-CN·C_6H_3Cl·NO_2 (**I**) and *p*-C_6H_4Me·SH (**II**) in EtOH at 70° affords 4-*chloro*-2-p-*tolylthiolbenzonitrile* (**III**), m.p. 117°; only a little Cl in (**I**) is replaced. (**III**) and H_2O_2–AcOH at 100° give 4-*chloro*-2-p-*toluenesulphonyl*-*benzonitrile* (**IV**), m.p. 187° [70% H_2SO_4 gives the corresponding *-benzoic acid* (**V**), m.p. 155°], and 4-*chloro*-2-p-*toluenesulphonylbenzamide*, m.p. 196° [30% H_2SO_4–aq. $NaNO_2$ or P_2O_5 at 200° yield (**V**) or (**IV**), respectively]. 1 : 2 : 4-CN·C_6H_3(NO_2)$_2$ and (**II**) as above give (mainly) 4-*nitro*-2-(**VI**), m.p. 156°, and 2-*nitro*-4-p-*tolylthiolbenzonitrile*, m.p. 115°, and thence 4-*nitro*-2- (**VII**), m.p. 176°, and 2-*nitro*-4-p-*toluenesulphonylbenzonitrile* (**VIII**), m.p. 201°, respectively. 1 : 2 : 4-CN·C_6H_3Cl·NO_2 (**IX**) [from 1 : 2 : 4-NH_2·C_6H_3Cl·NO_2 (modified prep.)] and (**II**) (as above or in NaOEt–EtOH) yield a mixture, m.p. 221—223°, of azoxy-, $C_{14}H_6ON_4Cl_2$, and azo-compound, $C_{14}H_6N_4Cl_2$. (**IX**) and excess of (**II**) in EtOH at 40°, treated slowly with 10% aq. NaOH, afford (**VI**) and 2-*chloro*-4-p-*tolylthiolbenzonitrile*, m.p. 95° [2-*chloro*-4-p-*toluenesulphonylbenzonitrile* (**X**), m.p. 175°]. (**VII**) or (**IV**) and (**II**) in boiling EtOH–dioxan–10% aq. NaOH yield 2-p-*toluenesulphonyl*-4-p-*tolylthiolbenzonitrile*, m.p. 132° (136° after some weeks). (**VIII**) or (**X**) similarly yields 4-p-*toluenesulphonyl*-2-p-*tolylthiolbenzonitrile*, m.p. 170°. In the above reactions, Cl or NO_2, but not CN, is replaced. (**I**) and piperidine afford 4-*chloro*-2-, m.p. 77°, and 2-*nitro*-4-*piperidinobenzonitrile*, m.p. 143°; the latter is also obtained similarly from 1 : 2 : 4-CN·C_6H_3(NO_2)$_2$. (**IX**) yields 4-*nitro*-2-*piperidinobenzonitrile*, m.p. 107°. (**IV**) or (**VII**) refluxed with piperidine for 3 or 30 min., respectively, gives 4-*piperidino*-2-, m.p. 198°, and (**VIII**) or (**X**) gives 2-*piperidino*-4-p-*toluenesulphonylbenzonitrile*, m.p. 150°. p-*Toluenesulphon*-2-*chloro*-4 : 6-*dinitroanilide*, m.p. 141°, is hydrolysed by 80% H_2SO_4 to 1 : 2 : 4 : 6-NH_2·C_6H_2Cl(NO_2)$_2$.

A. T. P.

Naphthalene derivatives from substituted γ-phenylcrotonic esters. L. Marion and J. A. McRae (*Canad. J. Res.*, 1940, **18**, B, 265—271).—Et α-carbethoxy-γ-phenyl-β-methyl-Δ^α-butenoate, one of the condensation products from CH_2Ph·COMe and CH_2(CO_2Et)$_2$ (method: Kon *et al.*, A., 1926, 1246; cf. A., 1930, 773), is hydrolysed to 1-*hydroxy*-3-*methyl*-*β*-*naphthoic acid* (**I**), m.p. 195° (decomp.). Decarboxylation (quinoline, Cu powder) of (**I**) gives 3 : 1-$C_{10}H_6Me$·OH (**II**), which by Kolbe synthesis affords (**I**). Et α-cyano-γ-phenyl-β-methyl-Δ^α-butenoate (*loc. cit.*), which does not undergo ring-closure on distillation, in glycerol at 240—250° (3 hr.) gives (probably) 1-*hydroxy*-3-*methyl*-*β*-*naphthonitrile*, m.p. 202°. (**II**) is synthesised by a method similar to that used by Veselý *et al.* (A., 1925, i, 804). M.p. are corr.

E. W. W.

Steroids. XXVII. Homologues of the testicular hormone. III. 20-Norpregnenolone. K. Miescher, F. Hunziker, and A. Wettstein [with, in part, C. Meystre] (*Helv. Chim. Acta*, 1940, **23**, 1367—1371; cf. A., 1940, II, 180).—Δ^5-Pregnene-3*t* : 20 : 21-triol 20 : 21-CMe_2 ether, m.p. 157—163° (Steiger *et al.*, A., 1938, II, 192), is hydrolysed to a mixture of Δ^5-pregnene-3*t* : 20 : 21-triols, m.p. 223—228°.



(*A*.)

This is transformed by aq. HIO_4 in dioxan and CO_2 at room temp. into Δ^5-*androsten*-3t-*ol*-17-*al* (20-*norpregnenolone*) (**I**) (*A*, R = H; R′ = CHO), a cryst. powder, m.p. 148—153° after transformation into rounded crystal forms at 130°, $[\alpha]_D^{21}$ −14·5°±4° in $CHCl_3$, which rapidly gives an intense aldehyde reaction with aq. NH_3–Ag_2O and an intense red coloration with 1 : 4-$C_{10}H_6$(OH)$_2$. If the HIO_4 fission is effected in MeOH instead of dioxan, the product is Δ^5-*androsten*-3t-*ol*-17-*al* *Me*$_2$ *acetal* [*A*, R = H; R′ = CH(OMe_2)], m.p. 185—189°, also obtained by the protracted action of 5% HCl–MeOH on (**I**) at room temp. (**I**) is converted by Ac_2O in C_5H_5N at room temp. into its *acetate*, m.p. 169—171°, $[\alpha]_D^{23}$ −13·5°±4° in $CHCl_3$, and is characterised by a *semicarbazone*, m.p. 226—228°, and a 2 : 4-*dinitrophenylhydrazone*, decomp. 207—209°. In 10—20-mg. doses 20-norprogesterone is now found to have slight progesterone activity. In the homologous series it is placed between androstenedione and progesterone; it shows the properties of both compounds in a slight degree. M.p. are corr. (vac.).

H. W.

Isomeric transformations of α-keto-alcohols. II. Acetylphenyl- and benzoylmethyl-carbinol. T. I. Temnikova (*J. Gen. Chem. Russ.*, 1940, **10**, 468—479).—MgPhBr and OH·CHMe·CN in Et_2O yield CHMeBz·OH (**I**), converted by heating with dil. HBr in MeOH (20 hr. at the b.p.), or with aq. $BaCO_3$ (20 hr. at 100°), into CHPhAc·OH (**II**). (**II**) is also obtained by reduction (Zn in 20% H_2SO_4) of Ph Me diketone. (**I**) and MgMeBr yield OH·CPhMe·CHMe·OH, also obtained, together with OH·CHPh·CMe_2·OH, from (**II**) and MgMeBr. (**I**) and MgPhBr afford chiefly OH·CPh_2·CHMe·OH, with some OH·CHPh·CPhMe·OH, which is the sole product obtained from (**II**). With BzCl, (**I**) gives CHMeBz·OBz, also obtained, together with some CHPhAc·OBz, from (**II**). The results point to the ready interconvertibility of (**I**) and (**II**), under the conditions of the various reactions, but do not afford evidence of tautomerism of the type (**I**) ⇌ (**II**).

R. T.

Effect of radicals on isomeric transformations of *tert.*-α-keto-alcohols. III. Effect of the α-naphthyl radical. A. M. Chaletzki (*J. Gen. Chem. Russ.*, 1940, **10**, 483—496).—1-$C_{10}H_7$·MgBr and COMe·CH_2Cl in Et_2O yield *α-chloro-β-1-naphthylpropan-β-ol*, an oil, decomp. at the b.p. COMeBu$^\gamma$ and $NaNH_2$ in Et_2O followed by 1-$C_{10}H_7$Br give *αβ*-dinaphthyl, but not the expected 1-$C_{10}H_7$·CH_2·COBu$^\gamma$. 1-$C_{10}H_7$·CH:CH_2 did not react with HBr in C_6H_6. 1-$C_{10}H_7$Ac is obtained in 75% yield by oxidation of 1-$C_{10}H_7$·CHMe·OH with CrO_3 in AcOH. 1-$C_{10}H_7$Ac with HCN in Et_2O at 0° yields *α-cyano-α-1-naphthylethyl alcohol*, decomp. 45°, which with MgBu$^\gamma$Cl in Et_2O gives *α-hydroxy-α-1-naphthylethyl Bu$^\gamma$ ketone*, b.p. 210—213°/3 mm., m.p. 168—169° (*semicarbazone*, m.p. 276—278°). This with dil. H_2SO_4–EtOH (8 hr. at 120°) gives *β-1-naphthyl-δδ-dimethyl-Δ$^\alpha$-penten-γ-one*, b.p. 198—199°/2 mm. (*semicarbazone*, m.p. 246—247°), which with MgMeBr gives *β-1-naphthyl-γδδ-trimethyl-Δ$^\alpha$-penten-γ-ol*, m.p. 139—140°.

R. T.

Photochemical transformation of *trans*- into *cis*-di-*p*-toluoylethylene.—See A., 1941, I, 54.

Nitration of the 3-halogeno-7-benzanthrones. F. H. Day (*J.C.S.*, 1940, 1474—1475).—3-Chloro- or -bromo-7-benzanthrone and 98% HNO_3 in $PhNO_2$ at 90—100° (bath) or 50°, respectively, afford 3-chloro-9-nitro- (I), m.p. 286°, or 3-bromo-9-nitro-7-benzanthrone, m.p. 298°, respectively; both are oxidised by CrO_3–aq. AcOH to 6-nitroanthraquinone-1-carboxylic acid, m.p. 277—278°. (I) and NH_2Ph,HCl–NH_2Ph–Zn dust at 120—140° yield the 9-NH_2-compound, m.p. 280—281°, converted (diazo-reaction) into 3 : 9-dichlorobenzanthrone, m.p. 267—268°, oxidised by CrO_3–aq. AcOH to 6-chloroanthraquinone-1-carboxylic acid, m.p. 305—306°. Relevant patent literature is reviewed.

A. T. P.

Δ$^{5:7:9}$-Œstratrien-3-ol-17-one, m.p. 138—139·5°, $[\alpha]_D$ +59° (acetate, m.p. 158° ; oxime, m.p. 195—197°), from urine of pregnant mares.—See A., 1940, III, 903.

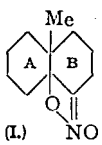
Corticosterone and its esters. M. H. Kuizenga and G. F. Cartland (*Endocrinol.*, 1940, **27**, 647—651).—The following esters (cf. Reichstein, A., 1937, II, 506) of corticosterone are prepared using the acid anhydride or chloride in C_5H_5N: acetate, m.p. 148—152°, *propionate*, m.p. 180—182°, butyrate, m.p. 168—169°, *hexoate*, m.p. 130—132°, *α-ethylbutyrate* (I), m.p. 179—180°, *heptoate*, m.p. 139—141°, palmitate, m.p. 82—84°, H succinate, m.p. 195—197°, and benzoate, m.p. 199—201°; (I) has the greatest biological activity (see A., 1940, III, 897).

H. B.

Steroids. XXVIII. Homologues of the testicular hormone. IV. Higher homologues of pregnenolone and progesterone. A. Wettstein (*Helv. Chim. Acta*, 1940, **23**, 1371—1379).—The reaction between Δ^5-3*t*-acetoxyætiocholenyl chloride (I) and $CHNa(CO_2Et)_2$ in C_6H_6 followed by hydrolysis and decarboxylation gives Δ^5-pregnen-3*t*-ol-20-one, m.p. 192—194°, $[\alpha]_D^{18}$ +30°±2° in EtOH (acetate, m.p. 149—150°, $[\alpha]_D^{20}$ +22°±2° in EtOH). Similar condensation of (I) with $CRNa(CO_2Et)_2$ (R = Me, Et, *iso*amyl) affords respectively Δ^5-21-*methyl*- (II), m.p. 170—171° (*acetate*, m.p. 175·5—176·5°), Δ^5-21-*ethyl*- (III), m.p. 125—127° (*acetate*, m.p. 114—115°), and Δ^5-21-iso*amyl*-, m.p. 136—138° (*acetate*, m.p. 142—143°), *-pregnen*-3t-*ol*-20-*one*. (II) is also prepared from (I) and $Mg[CMe(CO_2Et)_2]_2$ but a large proportion of (I) (isolable as Me Δ^5-3*t*-hydroxyætiocholenate) is unchanged. The prep. of (II) or (III) from (I) and $ZnEt_2$ or $ZnPr^\alpha I$ respectively is described. (II) and (III) are transformed by $Al(OPr^\beta)_3$ in PhMe–*cyclo*hexanone into 21-*methyl*-, m.p. 151—152°, and 21-*ethyl*-, m.p. 118—120°, *-progesterone*. Within the homologous series the pharmacological action diminishes more or less rapidly on both sides of progesterone. The next higher homologue is considerably more active than the next lower member and may be numbered with the small series of compounds with pronounced corpus luteum hormone action. M.p. are corr.

H. W.

Sugar-cane wax. VI. 6-Nitro-derivatives of sterols. VII. Oxidation of sugar-cane sitosterol. II. T. Mitui (*J. Agric. Chem. Soc. Japan*, 1940, **16**, 910—916, 917—924; cf. A., 1939, II, 504).—VI. Reduction of 6-nitrocholesteryl acetate with Zn dust and Et_2O–AcOH (1 : 1) gives *6-ketocholestanyl acetate oxime*, m.p. 200°, which with Zn dust and AcOH gives 6-ketocholestanyl acetate. The *oximes* of 6-keto-sitostanyl and 6-ketostigmastanyl acetate have m.p. 136° and 172°, respectively, and are similarly prepared from the NO_2-compounds. 6-Nitrocholestene with 5% MeOH–KOH or –NaOMe yields an isomeric *substance* (I), $C_{27}H_{45}O_2N$, m.p. 113°, similarly obtained from 3-chloro-6-nitrocholestene. An analogous *substance*, m.p. 152° (*acetate*, m.p. 96·5°; *benzoate*, m.p. 175°; 3 : 5-*dinitrobenzoate*, m.p. 158°), is prepared by alkali treatment of 6-nitrocholesteryl acetate or propionate, whilst 6-nitrostigmasteryl acetate yields a *substance*, m.p. 91—93°.

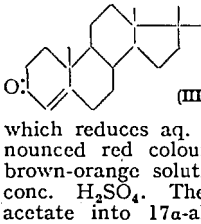


(I.)

VII. The hydroxy-ketone, m.p. 114°, obtained by oxidation (cf. A., 1938, II, 232) of sugar-cane sitosteryl acetate dibromide is 3-*hydroxynorcholesten*-24-*one* (II) (*acetate*, m.p. 167—168°), which is prepared from MgEtI and 3-*acetoxycholenamide*, m.p. 210—212°. Clemmensen reduction of (II) or 3-hydroxynorcholesten-25-one yields 3-*hydroxynorcholestene*, m.p. 132° (*acetate*, m.p. 120°). Me 3-acetoxycholenate with MgEtI yields the corresponding 3-*hydroxydiethylcarbinol*, m.p. 160—163° [3-*acetate* (III), m.p. 129·5°; *dichloride*, m.p. 116°, which with NaOPr gives *norsitostene*, m.p. 66—67°]. (III) with Ac_2O at 100° yields 3-*acetoxy*-Δ$^{5:6\cdot23:24}$-*norsitostadiene*, m.p. 117°, whilst with $SOCl_2$ it gives the *carbinyl chloride*, m.p. 130·5°, converted by NaOPr into 3-*hydroxynorsitostene*, m.p. 134·5° (*acetate*, m.p. 137°), reduction (PtO_2, H_2) of which yields 3-*hydroxynorsitostane*, m.p. 131—132° (*acetate*, m.p. 131°).

J. N. A.

Constituents of the adrenal cortex and related substances. XLI. Δ^4-Pregnene-17 : 20-diol-21-al-3-one 20-monoacetate. J. von Euw and T. Reichstein (*Helv. Chim. Acta*, 1940, **23**, 1114—1125; cf. A., 1940, II, 350).—Hydroxylation of the triene obtained from allyltestosterone gives (cf. Butenandt *et al.*, A., 1939, II, 76) 17-*αβγ*-trihydroxypropyltestosterone (I), m.p. 239—244°, and a (?) *diol*, m.p. 142—143°. (I), $COMe_2$, and anhyd. $CuSO_4$ at room temp. give 17-*α-hydroxy-βγ-isopropylidenedioxypropyltestosterone*, m.p. 235—236·5°, $[\alpha]_D^{18}$ +66·7°±2° in dioxan, which is transformed (Ac_2O in C_5H_5N at 60°) into the 20-*acetate*, m.p. 221—223°, $[\alpha]_D^{17}$ +107·4°±2° in $COMe_2$. This is hydrolysed by dil. AcOH to 17-*αβγ-trihydroxypropyltestosterone* 20-*monoacetate* (II), m.p. 210—211·5°, $[\alpha]_D^{18}$ +100·2°±2° in dioxan, also obtained by a similar sequence of changes from the product of the interaction of (I) and *cyclo*hexanone. HIO_4 in dioxan oxidises



(III.)

(II) to Δ^4-*pregnene*-17 : 20-*diol*-21-*al*-3-*one* 20-*acetate* (III), m.p. 206—208° (slight decomp.), $[\alpha]_D^{18}$ +119·1°±±3° in dioxan (*semicarbazone*, darkens and decomp. 190° without melting), which reduces aq. NH_3–Ag_2O at room temp., gives a pronounced red colour with 1 : 4-$C_{10}H_6(OH)_2$, and affords a brown-orange solution with a bright green fluorescence in conc. H_2SO_4. The conversion of *t*-dehydroandrosterone acetate into 17*α*-allylandrostenediol and its oxidation to 17*α*-allyltestosterone are fully described. The last compound is best dehydrated by $POCl_3$ in boiling C_5H_5N. It is hydroxylated (OsO_4) to 17-*βγ*-dihydroxypropyltestosterone-*a*, m.p. 226—231°, and -*b*, m.p. 190—195°, which when treated with anhyd. $CuSO_4$ and $COMe_2$ at room temp. yield 17-iso*propylidenedioxypropyltestosterone*-a, m.p. 135—136°, $[\alpha]_D^{15}$ +37·7°±2°, $[\alpha]_{5461}^{15}$ +45·2°±2° in $COMe_2$, and -*b*, m.p. 107—107·5°, $[\alpha]_D^{16}$ +61·0°±2°, $[\alpha]_{5461}^{16}$ +71·3°±2° in $COMe_2$ (also +0·5H_2O). From these compounds the pure triols (*b* has m.p. 207—207·5°) are obtained and are converted into their *dibenzoates*, m.p. 169—170° and 161—162°, respectively, but the corresponding acetates are non-cryst. Attempts to withdraw H_2O from these substances were unsuccessful. M.p. are corr.

H. W.

Constituents of the adrenal cortex and related substances. XLII. Partial synthesis of substance *S*. T. Reichstein and J. von Euw (*Helv. Chim. Acta*, 1940, **23**, 1258—1260).—Δ^4-Pregnene-17 : 20-diol-21-al-3-one 20-acetate is hydrolysed ($KHCO_3$ in aq. MeOH) to the non-cryst. aldehyde (I), which is extensively isomerised in boiling C_5H_5N to Δ^4-pregnene-17-21-diol-3 : 20-dione, m.p. 200—205° (corr.; decomp.). This is identical with substance *S* (II). It is further characterised by its acetate, m.p. 236—238° (corr.) after becoming opaque at 130°, $[\alpha]_D^{19}$ +116·33°±4° in $COMe_2$. Since (II) has the *β*-configuration at $C_{(17)}$ this must also be true for (I).

H. W.

Alkaline fusion. II. Reaction between anthraquinone and alkali. N. N. Voroshcov and A. P. Alexandrov (*J. Gen.*

Chem. Russ., 1940, **10**, 869—882).—Anthraquinone (**I**) does not react with aq. NaOH at room temp. (490 days). The products obtained from (**I**) and anhyd. NaOH (2 hr. at 274—276°) are BzOH, anthraquinol, and oxanthrone. With aq. NaOH at 275°, alizarin (**II**) and BzOH are produced, the yield of (**II**) rising with increasing $[H_2O]$. (**I**) and aq. NaOH–Na_2SO_3 (5·5 hr. at 210°) afford (**II**) and 2 : 10-*dihydroxy*-9-*keto*-2 : 9-*dihydroanthracene* (**III**) (*acetate*, m.p. 158—158·5°; *benzoate*, m.p. 192—193°), which decomposes at 274° to 2-hydroxyanthraquinone (**IV**) and dianthrone. (**III**) yields the same products when treated with C_6H_6 at the b.p., or with PbO_2 in xylene, and affords 2-methoxyanthraquinone with Me_2SO_4 or CH_2N_2. With aq. NaOH, (**III**) gives (**II**) and (**IV**). (**I**) and aq. NaOH–Na_2SO_3 at 235° yield (**II**), (**III**), and benzoylanthrone. R. T.

Organic cationoid reagents. R. Oda and U. Ueda (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1940, **38**, 44—49).—1-Nitroanthraquinone (**I**) in presence of conc. H_2SO_4 acts as a strong oxidising reagent (cationoid) with many org. compounds, whereby it is converted into 1-aminoanthraquinone (**II**) and 1-amino-4-hydroxyanthraquinone (**III**) (formed by rearrangement of the hydroxylamino-compound by H_2SO_4). Org. compounds readily oxidised at room temp. are α- and β-$C_{10}H_7$·OH, α-$C_{10}H_7$·NH_2, anthracene, acenaphthene, and carbazole; less readily oxidised are cresol, *p*-$C_6H_4(OH)_2$, 1-$C_{10}H_7Me$, tetrahydronaphthalene, anthrone, and unsaturated fatty oils; more difficultly oxidised are PhMe, PhOH, C_6H_4Me·NH_2, *m*-$C_6H_4(OH)_2$, $C_{10}H_8$, OH·$C_{10}H_6$·SO_3H, stilbene, and phenanthrene, whilst C_6H_6, PhCl, $PhNO_2$, BzOH, $COPh_2$, and PhCHO are not oxidised. Details are recorded for the interaction of (**I**), anthracene, and AcOH–H_2SO_4, to give (**II**), (**III**), and an impure, black oxidation–condensation product; a similar product is obtained using 1-nitroanthraquinone-sulphonic acid in place of (**I**), whereby the SO_3H-derivatives of (**II**) and (**III**) are formed. *o*-C_6H_4Bz·CO_2H (**IV**) also acts as a cationoid reagent in H_2SO_4 (ring-closure does not occur at room temp.); colour changes with various compounds are given. C_6H_6 and (**IV**) in conc. H_2SO_4 at 80° afford phthalophenone and anthraquinone; PhCl, BzOH, $PhSO_3H$, $PhNO_2$, and $C_{10}H_7$·SO_3H react with much difficulty or not at all. A. T. P.

Aminoanthraquinones.—See B., 1941, II, 7.

ω-Amino-derivatives of [quinones and] ketones. H. de Diesbach [with P. Lachat, M. Poggi, B. Baldi, R. Friderich, and H. Walker] (*Helv. Chim. Acta*, 1940, **23**, 1232—1252; cf. A., 1930, 607).—Condensation of 2 : 4-dimethylanthraquinone with the appropriate CH_2R·OH (*A*) (R = NH·CO·CCl_3 etc.) in conc. H_2SO_4 at 0° yields 2 : 4-*dimethyl*-1-*trichloroacetamidomethyl*- (**I**), m.p. 185°, and -1-*phthalimidomethyl*- (**II**), m.p. 199—200°, -*anthraquinone*. Reaction does not occur with NHBz·CH_2·OH. (**I**) is converted by boiling 30% KOH into NH_3, $CHCl_3$, and a mixture of aldehyde and alcohol oxidised by CrO_3 to pure 2 : 4-*dimethylanthraquinone*-1-*aldehyde* (**III**), m.p. 159°, which does not condense with NH_2OH or NHPh·NH_2 and does not give a violet colour with NH_2Ph in AcOH; it is oxidised by HNO_3 (*d* 1·15) at 220° to anthraquinone-1 : 2 : 4-tricarboxylic acid. Short treatment of (**I**) with boiling 10% NaOH–EtOH gives (**III**) accompanied by the very unstable 2 : 4-dimethyl-1-aminomethylanthraquinone (isolated as the *Bz* derivative, m.p. 160°) and αβ-2 : 2′ : 4 : 4′-*tetramethyl*-1 : 1′-*dianthraquinonylethylenediamine*; if the crude product is crystallised from quinoline instead of $PhNO_2$ *tetramethyldiisopyrroleanthrone* is isolated. NH_2·CH_2 is more stable in the hydroxyaminomethyl- than in the aminomethyl-anthraquinones. Condensation of phenanthraquinone and its derivatives in conc. H_2SO_4 at 0° with (*A*) occurs at $C_{(2)}$ and then at $C_{(7)}$. If a substituent is attached to $C_{(2)}$ reaction occurs at $C_{(7)}$. If OH is present at $C_{(2)}$ a second attack can occur at $C_{(3)}$. Thus are obtained 2-*chloroacetamidomethyl*-, m.p. 234°, 2-*trichloroacetamidomethyl*-, m.p. 203°, and 2-*phthalimidomethyl*-, m.p. 255°, 2 : 7-*di*(*trichloroacetamidomethyl*)- (**IV**), m.p. 238°, 2 : 7-*di*(*phthalimidomethyl*)-, m.p. >345°, 2-*nitro*-7-*trichloroacetamidomethyl*-, m.p. 215°, 2-*acetamido*-7-*phthalimidomethyl*-, m.p. >330°, 2-*hydroxy*-7-*benzamidomethyl*-, m.p. >290°, -7-*trichloroacetamidomethyl*-, m.p. ~200°, and -7-*phthalimidomethyl*-, m.p. 227°, 2-*hydroxy*-3 : 7-*di*(*trichloroacetamidomethyl*)-, decomp. ~190°, and -3 : 7-*di*(*phthalimidomethyl*)-, m.p. ~260° (decomp.), -*phenanthraquinone*. Hydrolysis (KOH) of these compounds gives NH_3 and probably compounds of high mol. wt.; thus (**IV**) affords a *substance*, $C_{32}H_{18}O_4N_2$. Condensation with benzanthrone occurs first at $C_{(3)}$ and then at $C_{(9)}$ but generally the disubstituted compound is obtained even when a deficiency of (*A*) is employed. NHBz·CH_2·OH is exceptional and enters only at $C_{(3)}$; if this position is occupied condensation does not occur. For other (*A*) entry is effected at $C_{(9)}$ if $C_{(3)}$ is substituted. Condensation is effected by cold, conc. H_2SO_4. The following are described: 3-*benzamidomethyl*-, m.p. 180°, oxidised by CrO_3 to anthraquinone; 3 : 9-*di*(*chloroacetamidomethyl*)-, m.p. 235°; 3 : 9-*di*(*phthalimidomethyl*)- (**V**), m.p. 285°; 3 : 9-*di*-(*trichloroacetamidomethyl*)-, m.p. ~235°, 3-*bromo*-, m.p. 247°, and 3-*nitro*-, m.p. 250°, -9-*trichloroacetamidomethyl*-; 3-*bromo*-9-*phthalimidomethyl*-, m.p. 257°, -*benzanthrone*. The position of the substituents is proved by the oxidation of (**V**) to 1-*phthalimidoacetyl*-6-*phthalimidomethylanthraquinone*, m.p. 260—265° (decomp.). Acenaphthenequinone and OH·CH_2·NH·CO·CCl_3 in conc. H_2SO_4 give 2-*trichloroacetamidomethylacenaphthenequinone*, m.p. 208°, oxidised by dil. HNO_3 to 1 : 2 : 3 : 5-$C_6H_2(CO_2H)_4$ (Me_4 ester, m.p. 108—109°). Fluorenone condenses immediately to 2 : 7-di-derivatives; if $C_{(2)}$ is occupied, entry occurs solely at $C_{(7)}$. The following are reported: 2 : 7-*di*(*benzamidomethyl*)-, m.p. 266°; 2 : 7-*di*(*chloroacetamidomethyl*)-, m.p. 259°; 2 : 7-*di*(*phthalimidomethyl*)-, m.p. >310°; 2 : 7-*di*(*trichloroacetamidomethyl*)- (**VI**), m.p. 248°, oxidised by HNO_3 (*d* 1·15) to fluorenone-2 : 7-dicarboxylic acid, m.p. 407° (Me_2 ester, m.p. 218°); 2-*nitro*-7-*mono*-, m.p. 211°, and -*tri*-*chloroacetamidomethyl*-, m.p. 190°; 2-*hydroxy*-, m.p. ~165°, and 2-*acetamido*-7-*trichloroacetamidomethyl*- (**VII**), m.p. 265°, -*fluorenone*. Xanthone condenses readily; thus by cautious working it is possible to obtain 2-*trichloroacetamidomethyl*-, whilst, by further substitution, (?) 2 : 4 : 5 : 7-*tetra*(*trichloroacetamidomethyl*)-, m.p. ~200° (decomp.), -*xanthone* is produced. Alkaline hydrolysis of acenaphthenequinone derivatives causes fission between the two CO whereas derivatives of fluorenone and xanthone yield NH_3 and polymerised products. Thus (**VI**) gives a *substance*, $C_{30}H_{22}O_4N_2$, m.p. >400°, and a *compound*, $C_{28}H_{21}O_3N_3$, m.p. >400°, is derived from (**VII**).

$COPh_2$ does not react with (*A*) but the presence of Me permits action, the position of Me governing that of the entering substituent. Thus *o*-C_6H_4Me·COPh affords 2-*methyl*-3 : 5-*di*(*phthalimidomethyl*)*benzophenone*, m.p. 198—200°, whilst *p*-C_6H_4Me·COPh yields 4-*methyl*-3-*phthalimidomethylbenzophenone*, m.p. 146·5°, and 2 : 4 : 1-$C_6H_3Me_2$·COPh affords 2 : 4-*dimethyl*-5-*trichloroacetamidomethyl*-, m.p. 163°, -5-*phthalimidomethyl*-, m.p. 147·5°, and -3 : 5-*di*(*phthalimidomethyl*)-, m.p. 233—235°, -*benzophenone*. If each C_6H_6 nucleus of $COPh_2$ contains one or more Me condensation takes place in both nuclei. Hydroxybenzophenones react readily giving diderivatives even in presence of a deficiency of (*A*); 2- (**VIII**), m.p. 116°, and 4-, m.p. 196°, -*hydroxy*-3 : 5-*di*(*trichloroacetamidomethyl*)*benzophenone* are described. Alkaline hydrolysis of these compounds gives NH_3 and polymerised products; thus (**VIII**) affords a *substance*, $C_{45}H_{42}O_8N_4$. The reactions established for anthraquinone are therefore repeated to a certain extent for other ketones and the changes must be ascribed to the CO groups.

o-C_6H_4Me·CO_2H gives 4-*benzamido*-, m.p. 191°, -*phthalimido*-, m.p. 226°, -*chloroacetamido*-, m.p. 152°, and -*trichloroacetamido*-, m.p. 244°, -*methyl*-*o*-*toluic acid*; these compounds are hydrolysed by conc. HCl to 4-*aminomethyl*-*o*-*toluic acid hydrochloride*, m.p. 244—245°. *p*-C_6H_4Me·CO_2H yields 2-*benzamido*-, m.p. 206°, -*phthalimido*-, m.p. 181°, -*chloroacetamido*-, m.p. 227·5°, and -*trichloroacetamido*-, m.p. 244°, -*methyl*-*p*-*toluic acid*. Hydrolysis (conc. HCl at ~180°) of these products affords 2-*aminomethyl*-*p*-*toluic acid hydrochloride*, m.p. 279—280°, converted by HNO_2 into 2-*hydroxymethyl*-*p*-*toluic acid*, m.p. 165°, which is oxidised by $KMnO_4$ to 1 : 2 : 4-$C_6H_3Me(CO_2H)_2$, m.p. 319—320°, and reduced by HI to 3 : 4 : 1-$C_6H_3Me_2$·CO_2H. *m*-C_6H_4Me·CO_2H gives 4-*phthalimidomethyl*-*m*-*toluic acid*, m.p. 261°, hydrolysed (conc. HCl) to 4-*aminomethyl*-*m*-*toluic acid hydrochloride*, m.p. 238°, transformed by the successive action of HNO_2 and $KMnO_4$ into 4 : 1 : 2-$C_6H_3Me(CO_2H)_2$. *m*-C_6H_4Me·CO_2H and OH·CH_2·NHBz in cold, conc. H_2SO_4 give 4-*methylphthalimidine*, m.p. 205° (*NO*-derivative, m.p. 225°). 2 : 4 : 1-$C_6H_3Me_2$·CO_2H affords 2 : 4-*dimethyl*-5-*trichloroacetamidomethylbenzoic acid*, m.p. 245°, hydrolysed to 2 : 4-*dimethyl*-5-*aminomethylbenzoic acid hydrochloride*, m.p. 284°, which gives 2 : 4-*dimethyl*-5-*hydroxymethylbenzoic acid*, m.p. 145°, oxidised to 4 : 6 : 1 : 3-$C_6H_2Me_2(CO_2H)_2$ (dichloride, m.p. 82—83°; diamide, m.p. 265—267°). H. W.

Composition and constitution of Turkey-red. H. E. Fierz-David and M. Rutishauser (*Helv. Chim. Acta*, 1940, **23**, 1298—1311).—Turkey-red (**I**) is a complex containing alizarin (**II**), Al, and Ca in the ratio 4 : 2 : 3; other substances do not appear to be present. It is readily prepared by prolonged heating of the three components (the metals in ionised form) in H_2O. This and similar lakes (*e.g.*, Fe^{III}, Cr) can be readily crystallised from H_2O–C_5H_5N, whereby a C_5H_5N complex is obtained. If this is heated at 130°/high vac. C_5H_5N and all H_2O excepting 2 mols. escape; these are so stably united that they are not expelled at 600°. The resulting complexes are black and on exposure to air absorb exactly 3 mols. of H_2O giving the colour lake, which probably has this composition on the fibre. Fatty substances used in dyeing with (**I**) probably serve to fix the metallic oxides as soaps on the fibre and then to bring the lake into the finest dispersion. Subsequently they separate from the complex which consists of (**II**), Al_2O_3, and CaO (4 : 2 : 3) with H_2O. In these lakes Ca can be replaced by other bivalent metals without marked alteration of the colour. The shade depends on the tervalent metal (Al, Fe, Cr). Treatment of (**I**) with $SnCl_2$ causes partial replacement of Ca but not of Al by SnO. Structures are suggested. H. W.

Biochemistry of the lower fungi. IV. Pigment of *Penicillium roseo-purpureum*, Dierckx. T. Posternak (*Helv. Chim. Acta*, 1940, **23**, 1046—1053; cf. A., 1940, II, 182).—The fungus is cultivated in the Czapek–Dox medium. The liquid is acidified with HCl and extracted with Bu$^{\beta}$OH after addition of NaCl; the mycelium is macerated with Bu$^{\beta}$OH. The combined extracts are heated with NaOH and the alkaline solution is acidified. BzOH is removed from the ppt., which, after purification through the acetate, gives *roseopurpurin* (**I**), $C_{16}H_{12}O_6$, m.p. 278—280° (decomp.; slowly heated), 285° (block). It gives a reddish-brown colour with $FeCl_3$; its variation in colour with p_H of its solutions is similar to that of 1 : 3-dihydroxyanthraquinone. The C_5H_5N salt forms orange needles. When distilled with Zn dust, (**I**) affords 2-methylanthracene. The presence of 3 OH in (**I**) is established by the isolation of a *triacetate*, m.p. 210°. The Me_3 derivative, m.p. 187°, of (**I**) is identical with tetramethylcitreorosein (*loc. cit.*). Oxidation of (**I**) by $KMnO_4$ first in alkaline and then in acid solutions leads to *anisole-2 : 3 : 5-tricarboxylic acid* (**II**), m.p. 251° (gas evolution) and 250° after re-solidification (*anhydride*, m.p. 252°). 1 : 3 : 4 : 5-$C_6H_2Me_2Ac{\cdot}OMe$ is oxidised by aq. $KMnO_4$ to 3-*methoxy-5-carboxyphthalonic acid*, m.p. ~240° (decomp.), further oxidised in acid solution to (**II**). (**I**) is therefore 5 : 7-*dihydroxy-4-methoxy-2-hydroxymethylanthraquinone*. H. W.

Biochemistry of micro-organisms. LXVIII. Synthesis of cynodontin (1 : 4 : 5 : 8-tetrahydroxy-2-methylanthraquinone), a metabolic product of species of *Helminthosporium*. W. K. Anslow and H. Raistrick (*Biochem. J.*, 1940, **34**, 1546—1548).—The benzoylbenzoic acid obtained from 3 : 6 : 4 : 1 : 2-$(OMe)_2C_6HMe(CO)_2O$, *p*-$C_6H_4(OMe)_2$, and $AlCl_3$ in CS_2, is cyclised and demethylated by conc. H_2SO_4 at 150° (bath) to 1 : 4 : 5 : 8-*tetrahydroxy-2-methylanthraquinone*, m.p. 260—261° (when purified through the *tetra-acetate*, m.p. 224—226°), identical with cynodontin (A., 1933, 1082). P. G. M.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Biochemistry of micro-organisms. LXVI. Penicilliopsin, the colouring matter of *Penicilliopsis clavariæformis*, Solms-Laubach. A. E. Oxford and H. Raistrick (*Biochem. J.*, 1940, **34**, 790—803).—The fungus, when grown in the dark at 24° (best on an orange-extract medium), produces a cryst. colouring matter *penicilliopsin* (**I**), $C_{30}H_{24}O_8$, orange-red, m.p. 330° (decomp.) [*bisphenylcarbamate*, yellow, m.p. 238—240° (decomp.); *diacetate*, orange-yellow, decomp. above 280°]. With CH_2N_2 (**I**) gives a *compound*, $C_{34}H_{32}O_8$ (*i.e.*, $C_{30}H_{24}O_8 + 4CH_2$), orange-yellow, m.p. 340—360° (decomp.), OMe nil by Zeisel. $CHMeN_2$ affords the *isomeride* ($C_{36}H_{24}O_8 + 2C_2H_4$), yellow, m.p. ~310°, OEt nil by Zeisel. When heated alone or with Zn dust (**I**) gives *Frangula*-emodin anthranol. Distillation with Zn dust in H_2 affords 2-methylanthracene. Oxidation of (**I**) with HNO_3 yields tetranitro-*Frangula*-emodin, nitrococcusic acid, and $H_2C_2O_4$. (**I**) is oxidised in air in org. solvents in presence of org. bases to *oxypenicelliopsin* (**II**), $C_{30}H_{20}O_9$, purple-black, m.p. above 360° [*tetra*(?)-*acetate*, orange-red, m.p. 308—310° (decomp.)]. Solutions of (**II**) when exposed to light are converted into an *isomeride* (**III**), chocolate-brown, m.p. above 370°, giving intensely fluorescent solutions. (**III**) is closely related to hypericin derived from *Hypericum perforatum*. The absorption and fluorescence spectra of the two substances are indistinguishable (Dhéré and Castelli, A., 1939, III, 1007) but chemical reactions prove their non-identity. The substance "mycoporphyrin" obtained from naturally occurring *P. clavariæformis* was probably a mixture of (**I**), (**II**), and (**III**). (**I**) may be a polyhydroxy-derivative of a reduced *meso*dimethyldianthrone. J. H. B.

Sterols. CVII. Steroidal sapogenins of *Alestris*, *Asparagus*, and *Lilium*. R. E. Marker, D. L. Turner, A. C. Shabica, E. M. Jones, J. Krueger, and J. D. Surmatis (*J. Amer. Chem. Soc.*, 1940, **62**, 2620—2621).—*Alestris farinosa*, L., yields diosgenin. *Asparagus officinalis*, L., yields sarsasapogenin. *Lilium rubrum magnificum* yields *liligenin*, $C_{27}H_{44}O_4$, m.p. 245—246° (digitonide; *diacetate*, m.p. 158°), which with CrO_3–AcOH at 25° gives only acids and is thus a 2 : 3- or 3 : 4-diol. R. S. C.

Isomerides of bixin and methylbixin. Synthesis of dihydrobixin from dihydromethylbixin. T. Takahashi (*J. Pharm. Soc. Japan*, 1936, **56**, 352—355).—Bixin (**I**) and 3% HCl in MeOH give methylbixin. Labile (**I**) is apparently converted into the stable form by oxidising with BzO_2H and reducing the resulting compound, m.p. 216—217°. Dihydrobixin, m.p. 207—208° (cf. A., 1929, 1075), and dihydromethylbixin, m.p. 178°, are also described. Ch. Abs. (*c*)

Ultra-violet absorption spectra of lignin and related compounds.—See A., 1941, I, 27.

V.—HETEROCYCLIC.

Secondary and tertiary arylamines containing the furfuryl group. I. Furfurylaniline and furfurylethylamine. A. I. Umnova (*J. Gen. Chem. Russ.*, 1940, **10**, 569—576).—Furfurylideneaniline is reduced (Zn in aq. NaOH; 8 hr. at 75°) to *furfurylaniline* (**I**), b.p. 147—148°/10 mm. (*hydrochloride*; *oxalate*), from which *furfurylphenylnitrosoamine*, m.p. 28°, is obtained. (**I**) yields an azo-dye, $CH_2R{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}SO_3Na$ (R = 2-furyl), with *p*-$SO_3Na{\cdot}C_6H_4{\cdot}N_2Cl$ (**II**). $NaNH_2$ and a solution of (**I**) in Et_2O–EtBr yield *furfurylethylaniline* (**III**), b.p. 147—147·5°/11 mm. This gives p-*nitrosofurfurylethylaniline*, m.p. 75—76°, with HNO_2. With PhCHO in presence of 30% HCl (**III**) yields an analogue of malachite-green, and with (**II**) gives an analogue of helianthin. R. T.

Further homologue of α-tocopherol. P. Karrer and O. Hoffmann (*Helv. Chim. Acta*, 1940, **23**, 1126—1131).—3 : 5 : 1-$C_6H_3MeEt{\cdot}OH$ is transformed by boiling C_6H_6–AcCl into the acetate, b.p. 126—128°/15 mm., which is converted by $AlCl_3$ at 160—170° into a mixture of 2-*hydroxy*-4(6)-*methyl*-6(4)-*ethylacetophenones*, m.p. 93°, and b.p. 144°/12 mm., m.p. 18—19°, separated from one another through the *semicarbazones*, m.p. 228° and 193°. They are reduced (Zn–Hg and HCl) to the corresponding *methyldiethylphenols*, m.p. 121—123°/13 mm., and (**I**), b.p. 121—123°/12 mm. (**I**) in EtOH–conc. HCl with $NaNO_2$ at 0° gives 4-*nitroso*-3(? 5)-*methyl*-2 : 5(? 2 : 3)-*diethylphenol*, m.p. 150° (decomp.), converted by $NaNO_2$ and 7·5% HCl into 5(? 3)-*methyl*-2 : 3(? 2 : 5)-*diethyl*-1 : 4-*benzoquinone*, b.p. 94—99°/0·4—0·6 mm., which is reduced to the *quinol*, m.p. 141—142°. This is condensed ($ZnCl_2$ in boiling C_6H_6) with phytyl bromide to dl-7(? 5)-*methyl*-5 : 8(? 7 : 8)-*diethyltocol*, a pale yellow viscous liquid with marked reducing power (*allophanate*, m.p. 166°) which has full vitamin-*E* activity in 10-mg. doses. H. W.

Unsaturated derivative of the tocopherol series (? *dl*-Δ^3-dehydro-α-tocopherol). P. Karrer, R. G. Legler, and G. Schwab (*Helv. Chim. Acta*, 1940, **23**, 1132—1137).—γηλο-Tetramethyl-Δ$^{\alpha}$-hexadecinen-γ-ol (**I**) is transformed by PBr_3 in light petroleum at −15° into a mixture of bromides (very predominatingly γ-bromo-γηλο-tetramethyl-Δ$^{\alpha}$-hexadecinene) which condenses with trimethylquinol (**II**) in C_6H_6 or light petroleum containing $ZnCl_2$ to (?) *dl*-Δ^3-dehydro-α-tocopherol (**III**) (*allophanate*, m.p. 163°) in very poor yield. (**III**) is reduced (Pt in EtOH) to a substance (allophanate, m.p. 172°) very similar to or identical with *dl*-α-tocopherol. Attempts to improve the yield of (**III**) by purification through the acetate, b.p. 170°/0·01 mm., were unsuccessful. (**III**) is also

obtained in small yield by condensing (I) with (II) in presence of $ZnCl_2$ at 175°. H. W.

***dl*-α-Tocopherolphosphoric ester.** P. Karrer and G. Bussmann (*Helv. Chim. Acta*, 1940, **23**, 1137—1138).—*dl*-α-Tocopherol (I) is readily converted by $POCl_3$ in anhyd. C_5H_5N at 0° into the H_2 phosphate, isolated as the Na_2 salt. This is remarkably resistant to hydrolysis but its vitamin-*E* activity is equal or superior to that of (I). It is not hydrolysed by kidney-, serum-, or yeast-phosphatase. H. W.

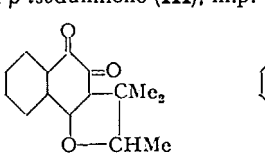
α-Tocopheryl 3-bromocamphorsulphonate.—See B., 1941, III, 21.

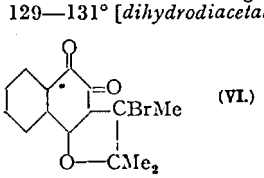
Catalytic hydrogenation of coumarone. N. I. Schujkin, I. I. Dmitriev, and T. P. Dobrinina (*J. Gen. Chem. Russ.*, 1940, **10**, 967—972).—The chief product of hydrogenation of coumarone with Pd catalyst at 175° is octahydrocoumarone, with 2-ethyl*cyclo*hexanol (I) and β-*cyclo*hexylethanol as by-products. With Ni catalyst the chief product is (I). The same products are obtained with Pt catalyst in EtOH at 50°. R. T.

Benzopyrylium salts. II. Ozonisation. R. L. Shriner and R. B. Moffett (*J. Amer. Chem. Soc.*, 1940, **62**, 2711—2714; cf. A., 1939, II, 385).—4′-Bromo-3-methoxyflavylium chloride and O_3 in AcOH give *o*-OH·C_6H_4·CHO (I), *p*-$C_6H_4Br·CO_2H$ (II), and *Me* o-p′-*bromobenzoyloxyphenyl acetate*, m.p. 87—88° [hydrolysed by 25% KOH to (II) and *o*-OH·C_6H_4·CH_2·CO_2H]. 4′-Bromo-3-phenylflavylium chloride (III) [prep. from (I) and *p*-$C_6H_4Br·CO·CH_2Ph$ and HCl in dioxan; corresponding *ferrichloride* (IV), m.p. 162—163·5°] and O_3 in AcOH give (I), 4-bromobenzil (V), and (II). Boiling KOH–EtOH converts (IV) into 2-*ethoxy*-3-*phenyl*-2-p-*bromophenyl*-1 : 2-*benzpyran*, m.p. 101—102·5°, obtained also from (III) by EtOH at 0°, and converted by O_3 in CCl_4 into (V), (I), (II), and EtOH. Pyrylium salts thus undergo cleavage at positions 2 : 3 and 3 : 4 and are best considered as $C_{(2)}$ and $C_{(4)}$ carbenium salts. R. S. C.

Benz-furans and -pyrans.—See B., 1941, III, 21.

Dunnione. II. J. R. Price and (Sir) R. Robinson (*J.C.S.*, 1940, 1493—1499; cf. A., 1939, II, 557).—Dunnione (I) (phenyleneazine, $[\alpha]_D^{16}$ +237° in $CHCl_3$) (improved method of isolation) is *aaβ*-trimethyldihydrofurano-1 : 2-naphthaquinone (*loc. cit.*). α-Dunnione (II), $[\alpha]_D^{19}$ +104° in $CHCl_3$ (*dihydrodiacetate*, m.p. 119—121°, $[\alpha]_D^{18}$ +80·4° in $CHCl_3$), is the isomeric 1 : 4-naphthaquinone. (I) or (II) (Kuhn–Roth oxidation) affords 1·3 or 1·04 mols. of AcOH, respectively. (I) and H_2SO_4 at room temp. for 72 hr., then at 100° for 2 hr., give <5% of β-*iso*dunnione (III), m.p. 129—131° [*dihydrodiacetate*,





m.p. 119—121°; *semicarbazone*, m.p. 218—219° (decomp.); *phenyleneazine* (IV), m.p. 118—120°], which is probably *aββ*-trimethyldihydrofurano-1 : 2-naphthaquinone. (I) and $K_2C_2O_7$–aq. H_2SO_4 afford $COMePr^{\beta}$ (2 : 4-dinitrophenylhydrazone, new m.p. 122—123°). (III) similarly, or by H_2O_2–aq. NaOH, yields $COMe_2$. α-*iso*Dunnione, m.p. 118—119° (*dihydrodiacetate*, m.p. 135—136°; *semicarbazone*, m.p. 222—223°), and conc. H_2SO_4 at room temp. afford (III). The *iso*dunniones resemble the lapachones more closely than they do (I) or (II). A solution of (III) in 1—5% aq. NaOH, made faintly acid and kept at 0° for 2—3 hr., yields *hydroxyhydro*-iso*dunniol* (V), m.p. 112—113° (*dihydrotetra-acetate*, m.p. 183—184°). With *o*-$C_6H_4(NH_2)_2$ in AcOH, (V) affords (III) + (IV), but in EtOH + a little AcOH, it gives a *product*, $C_{21}H_{20}O_2N_2$, m.p. 193—194°, converted by H_2SO_4 into (IV). (V) and alkaline $KMnO_4$ give (III) only. The corresponding hydroxyhydrodunniol could not be obtained from (I) or (II) owing to its sensitivity to alkalis [which afford (VII)] and to acids (effect ring-closure). (III) and Br–$CHCl_3$ at room temp. (4—6 days) give *bromo*-β-iso*dunnione* (VI), m.p. 141—143° (α-bromo-*aββ*-trimethyldihydrofurano-1 : 2-naphthaquinone), whereas (I) does not react with Br–$CHCl_3$ at 55°. (VI) in Zn–aq. NaOH (2 hr.), and air drawn through for 2 hr., afford *iso*dunniol, m.p. 118—119° [H_2SO_4 gives (III)], which is possibly 3-trimethylvinyl-2-hydroxy-1 : 4-naphthaquinone. The structure of *allo*dunnione (VII) is not clear. (VII) is oxidised by CrO_3 to $COMe_2$ and reduced by Sn–HCl or Zn–AcOH to a H_2-compound, m.p. 141—142° (Ac_2O–NaOAc give the *diacetate*, m.p. 191—193°), or by Zn–10% aq. NaOH to *dihydrohydroxyhydro*allo*dunnione*, m.p. 160—161° (presumably due to opening of a lactone, coumaran, or chroman ring). (VII) and conc. H_2SO_4 at 100° give a *sulphonic acid*, $C_{15}H_{14}O_6S$. A. T. P.

Reactions of organic α-oxides with alcohols and compounds containing the carbonyl group, in presence of boron fluoride. A. A. Petrov (*J. Gen. Chem. Russ.*, 1940, **10**, 981—996).—Alcohols with oxides in presence of BF_3 yield ethers: $(CH_2)_2O$ + MeOH → OH·$[CH_2]_2$·OMe. Aldehydes react similarly with oxides, giving dioxolans; thus $(CH_2)_2O$ + CORR′ → $\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}$>CRR′ (R = Me, R′ = Me, *Et*, b.p. 118—118·5°, Pr$^{\alpha}$, b.p. 140—140·5°). OH·CH_2·CH(OH)·CH_2Cl and $COMe_2$, COMeEt, or COMePr yield similarly 4-chloromethyl-2 : 2-dimethyl-, -2-*methyl*-2-*ethyl*-, b.p. 174—177°, or -2-*methyl*-2-*propyl*-*dioxolan*, b.p. 192—196°. Me βγ-oxidopropyl ether reacts similarly with these ketones, affording 4-*methoxymethyl*-2 : 2-*dimethyl*, b.p. 154—155·5°, -2-*methyl*-2-*ethyl*-, b.p. 171·5—173°, and -2-*methyl*-2-*propyl*-*dioxolan*, b.p. 188—191°. $(CHMe)_2O$ and PrCHO yield 4 : 5-*dimethyl*-2-*propyldioxolan*, b.p. 155—157°, and with $COMe_2$, COMeEt, or COMePr the products are 2 : 2 : 4 : 5-tetramethyl-, 2 : 4 : 5-trimethyl-2-ethyl-, and 2 : 4 : 5-*trimethyl*-2-*propyl*-*dioxolan*, b.p. 161—163°. *iso*Butylene oxide and $COMe_2$ yield 2 : 2 : 4 : 4-*tetramethyldioxolan*, b.p. 109—110°. Hexene oxide and $COMe_2$, COMeEt, or COMePr similarly afford 2 : 2-dimethyl-, 2-*methyl*-2-*ethyl*-, b.p. 96—98°/25 mm., or 2-*methyl*-2-*propyl*-*benzdioxolan*, b.p. 111·5—113·5°/25 mm. R. T.

Splitting of pyrrolidine derivatives by cyanogen bromide. E. Ochiai and K. Tsuda (*J. Pharm. Soc. Japan*, 1936, **56**, 357—359).—*N*-Amylpyrrolidine and BrCN in C_6H_6 at 100° form *N-amylpyrrolidine bromocyanide*, b.p. 135°/0·016 mm., the non-basic reduction product of which (H_2–Pd–$CaCO_3$ in KOH–MeOH) when treated with 30% H_2SO_4 yields the *hydrochloride*, $C_9H_{22}NCl$, m.p. 285° (*Pt* salt, m.p. 179°; *Au* salt, m.p. 172°), of *N*-butylamylamine. Similarly, *N*-*iso*amylpyrrolidine gave *N*-butyl*iso*amylamine. Ch. Abs. (*c*)

Action of organometallic compounds on dimethylmaleic anhydride. D. S. Tarbell and C. Weaver (*J. Amer. Chem. Soc.*, 1940, **62**, 2747—2750).—(CMe·CO)$_2$O and MgPhBr (2 mols.) in PhMe give *β-benzoyl-α-phenyl-α-methyl*-n-*butyric acid*, *forms*, (I) m.p. 185°, and (II) m.p. 113° (cf. A., 1938, II, 102). Either form with $SOCl_2$, followed by $NaNH_2$, gives 2-*keto*-3 : 5-*diphenyl*-3 : 4-*dimethyl*-2 : 3-*dihydropyrrole*, m.p. 67—69°, and, when distilled at 245—250°, gives 2-*keto*-3 : 5-*diphenyl*-3 : 4-*dimethyl*-2 : 3-*dihydrofuran* (III), m.p. 67—68°. Dissolution of (III) in NaOH and then acidification gives (I). Ozonisation of (III) gives 83% of BzOH. 78% of BzOH is obtained from (I) by boiling $K_2Cr_2O_7$–H_2SO_4–AcOH. Martin–Clemmensen reduction of (I) gives *αγ-diphenyl-α-methyl*iso*valeric acid*, m.p. 177—178°. COPh·CMe:CMe·CO_2H (IV) and MgPhBr (>2 mols.) in Et_2O give (I) and (II) (total 85·5%). (CMe·CO)$_2$O is converted by ZnPhCl in boiling C_6H_6 into (IV) (83%) and by LiPh (2 mols.) in Et_2O into 2-*keto*-5 : 5-*diphenyl*-3 : 4-*dimethyl*-2 : 5-*dihydrofuran* (67·5%), m.p. 89—90° (with CrO_3 gives 72% of $COPh_2$), also obtained from (IV) by LiPh (2 mols.). R. S. C.

***N*-Cyanomethylpyrrole and its Hoesch reaction.** E. Ochiai and S. Ikuma (*J. Pharm. Soc. Japan*, 1936, **56**, 379—381).—K pyrrole and $CH_2Cl·CN$ in C_6H_6 give *N-cyanomethylpyrrole*, b.p. 84—87°/4 mm., which is hydrolysed to the amide (Clemo, A., 1931, 365) by H_2O at 120—130° and with HCl in Et_2O gives a *ketone*, C_6H_5ON or $C_{12}H_{10}O_2N_2$, m.p. 307—308° (semicarbazone, m.p. 273°) (structures suggested). Ch. Abs. (*c*)

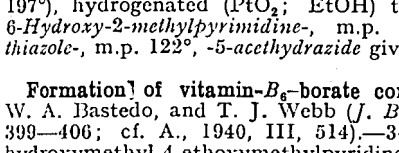
Derivatives of pyrrolidine and piperidine. K. Tsuda (*J. Pharm. Soc. Japan*, 1936, **56**, 359—360).—2 : 6-Lutidine methiodide is converted into the methochloride with AgCl and then reduced (Pt–H_2 in AcOH at 2 atm.) to 1 : 2 : 6-*trimethylpiperidine*, b.p. 65—70°/55 mm. (*picrate*, m.p. 228°; *Au* salt, m.p. 162°). K 2-methylpyrrole and BuBr give 2-*methyl*-1-*butylpyrrole*, b.p. 110—115°/28 mm., which when reduced as above affords 2-*methyl*-1-*butylpyrrolidine*, b.p. 85—88°/57 mm. (*hydrochloride*, m.p. 168°; *methiodide*, m.p. 207°; *picrate*, m.p. 122°). Ch. Abs. (*c*)

Pyrimidines related to vitamin-B_1. I. New synthesis of 6-amino-2-methylpyrimidine-5-aldehyde. D. Price, (Miss)

E. L. May, and F. D. Pickel (*J. Amer. Chem. Soc.*, 1940, **62**, 2818—2820).—Addition of MeOH–H_2SO_4 to 6-*amino*-2-*methylpyrimidine*-5-*carboxylic acid* (prep. from the 5-CN-derivative by 10% KOH), m.p. 270—270·5° (decomp.) (*hydrochloride*, m.p. 238—239°), in conc. H_2SO_4 (no other method) gives the *Me* ester, m.p. 184—184·5° (*hydrochloride*, m.p. 181°), which with N_2H_4,H_2O in boiling aq. EtOH gives the *hydrazide*, m.p. 220—221° (decomp.). The *PhSO*$_2$ derivative, m.p. 228·5—229° (decomp.), thereof with Na_2CO_3 in $(CH_2{\cdot}OH)_2$ at 157—160° gives 6-amino-2-methylpyrimidine-5-aldehyde, m.p. 195—196° (lit. 192°) (p-$C_6H_4Me{\cdot}N$: derivative, m.p. 196—197°), hydrogenated (PtO_2; EtOH) to the alcohol (70%). 6-*Hydroxy*-2-*methylpyrimidine*-, m.p. 238°, and 4-*methylthiazole*-, m.p. 122°, -5-*acethydrazide* give no aldehyde.

R. S. C.

Formation of vitamin-B_6–borate complex. J. V. Scudi, W. A. Bastedo, and T. J. Webb (*J. Biol. Chem.*, 1940, **136**, 399—406; cf. A., 1940, III, 514).—3-Hydroxy-2-methyl-5-hydroxymethyl-4-ethoxymethylpyridine and 3-hydroxy-2-methyl-4 : 5-oxidodimethylpyridine condense with 2 : 6-dichlorobenzoquinone chloroimide in presence of borate buffer.



(I.)

The shift in the absorption spectrum of vitamin-B_6 on passing from p_H 3 to 7·5 is eliminated by addition of borate. Electrometric titration curves of -B_6 and H_3BO_3 separately and together show that the complex contains 2 mols. of -B_6 to 1 of H_3BO_3. Formula (**I**) is proposed for the complex, which is as physiologically active as the vitamin, and is thermostable in neutral solution.

A. Li.

Reduction of 1-acetyl-2-methylindolidine. E. Ochiai and E. Kobayashi (*J. Pharm. Soc. Japan*, 1936, **56**, 376—378).—Reduction of 1-acetyl-2-methylindolidine (H_2 at 2·3 atm., PtO_2 in AcOH) affords 2-methyl-1-ethylindolizidine, and a *compound*, $C_{11}H_{21}ON$, b.p. 102—103°/6 mm., probably 2-methyl-1-α-hydroxyethylindolizidine (*phenylurethane*, m.p. 137°; *acetate*, b.p. 110—111°/6 mm.). Ch. Abs. (*c*)

Preparation of 2-aldopolyhydroxyalkylbenziminazoles. S. Moore and K. P. Link (*J. Org. Chem.*, 1940, **5**, 637—643).—Direct oxidative condensation of aldo-monosaccharides with *o*-$C_6H_4(NH_2)_2$ gives low yields of benziminazole derivatives but if $Cu(OAc)_2$ is added the yield of galactobenziminazole increases to 40% whereas the results with glucose are poor. By effecting the reaction in dil. AcOH at 50° for 12 hr. the yield of glucobenziminazole (**I**) is raised to 25% but side reactions remain prominent. Concn. of the solution of an aldonic acid and a slight excess of *o*-$C_6H_4(NH_2)_2$ to a syrup in presence of HCl and H_3PO_4 at 135° gives 60—80% yields of aldobenziminazoles from arabonic, galactonic, gluconic, lyxonic, mannonic, and rhamnonic acid. Under these conditions xylonic acid does not give a benziminazole derivative with production of the *compound*, $C_{11}H_{16}O_5N_2$, m.p. 140—141° (*picrate*, m.p. 187—189°), but one equiv. of *o*-$C_6H_4(NH_2)_2$ reacts; at 180° in the presence of an acid catalyst (best $ZnCl_2$ and HCl) xylobenziminazole, m.p. 224°, is produced. The 2-aldopolyhydroxyalkylbenziminazoles are amphoteric compounds. H attached to *sec.* N is weakly acidic and aldobenziminazoles dissolve in excess of a strong base such as NaOH but not in aq. NH_3. They may be pptd. by CO_2 from solution in NaOH. Ammoniacal Ag, Cu, and Zn solutions cause the formation of insol. complex salts. In the absence of excess of aq. NH_3 the pptn. of aldobenziminazoles as Cu salts is quant. The *sec.* N can be alkylated. CH_2PhBr and (**I**) in aq. EtOH at 100° afford 1-*benzyl*-2-d-*glucopentahydroxyamylbenziminazole*, m.p. 188°, $[\alpha]_D^{25}$ +37·0°. The use of these compounds in the characterisation of carbohydrates is suggested. H. W.

Nucleic acid of rye ergot. II. M. Gatty-Kostyal and J. Tesarz (*Wiadom. Farm.*, 1936, **63**, 213—216, 229—233, 245—249; cf. A., 1934, 709).—Nucleic acid (**I**) from rye ergot contains P 8·30—8·46, N 14·63—15·47% (P : N = 1·75—1·84) and after twofold hydrolysis with H_2SO_4 and pptn. with Ag_2O, 10·87% of purine-N (10·12 N : 4 P). The isolation of adenine (*picrate*, m.p. 294° with decomp.), guanine (the sulphate gives the xanthine but not the Kossel test), cytosine [*picrate*, m.p. 265—266° (decomp.)], and uracil is described but xanthine and hypoxanthine could not be isolated in quantity. Of sugars only *d*-ribose and *d*-2-deoxyribose are present so that the constitutions of ergot-(**I**) and yeast-(**I**) are similar. Ch. Abs. (*c*)

Variation of the magnetic susceptibility of hæmin in various solvents.—See A., 1941, I, 33.

Morpholinomethyl ketones. J. P. Mason and S. D. Ross (*J. Amer. Chem. Soc.*, 1940, **62**, 2882—2883).—Morpholine (2 mols.) and the appropriate chloroketone (1 mol.) in Et_2O at room temp. give *morpholinoacetone*, b.p. 101—101·5°/14 mm. (*hydrochloride*, m.p. 183°; *picrate*, m.p. 145·5°), and α-*morpholinobutan*-β-*one*, b.p. 97—100°/9 mm. (*hydrochloride*, m.p. 171—172·5°; *picrate*, m.p. 127—129°). ω-*Morpholinoacetophenone*, m.p. 50—52° [hydrochloride, m.p. 212—214° (lit. 222—223°); *picrate*, m.p. 156—157°], and -p-*phenylacetophenone*, m.p. 113—114° (*hydrochloride*, m.p. 233—235°; *hydrobromide*, m.p. 233—234°; *picrate*, m.p. 160—162°), and p-*bromo*-ω-*morpholinoacetophenone*, m.p. 88·5—89° [*hydrochloride*, m.p. 218° (decomp.); *picrate*, m.p. 145—146°], are prepared by the method of Rubin *et al.* (A., 1940, II, 143).

R. S. C.

Tautomeric compounds. I. *iso*Oxazolone and oxazolone derivatives. A. E. Porai-Koschitz and N. V. Chromov (*J. Gen. Chem. Russ.*, 1940, **10**, 557—568).—OH·N:CMe·$CH_2{\cdot}CO_2Et$ (**I**) and Na at 80° give 3-methyl*iso*oxazolone (**II**), in 50% yield. In C_6H_6 or EtOH solution (**II**) exists only in the anhydride form, as 5'-hydroxy-3 : 3'-dimethyl-4' : 5-di*iso*oxazolyl. Attempted condensation of (**II**) with aldehydes was unsuccessful. (**I**) and *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ (**III**) afford 4-p-*dimethylaminobenzylidene*-3-*methylisooxazolone* (**IV**), m.p. 203—204°, which in alkali gives p-*dimethylaminophenyldi*-(3-*methylisooxazolonyl*)*methane* (**V**) and (**III**); this reaction is reversed by acidifying. In acid solutions (**V**) yields (**IV**) and (**II**). A solution in Ac_2O of (**III**), hippuric acid, and NaOAc heated for 30 min. at 100° yields 2-p-*dimethylaminobenzylidene*-4-*phenyloxazolone*, m.p. 216·5—217°.

R. T.

Metallation of phenoxthionine. H. Gilman, (Miss) M. W. van Ess, H. B. Willis, and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1940, **62**, 2606—2611).—Phenoxthionine (**I**) and LiBu^a in Et_2O give the 4-Li derivative, which with CO_2 gives *phenoxthionine*-4-*carboxylic acid* (**II**) (61%), m.p. 168—169° [10-*dioxide*, m.p. 183—184°; *Me* ester, m.p. 124°; *amide* (**III**), m.p. 185—186°; with Cu-bronze in quinoline at 200° gives (**I**)]. 4-*Aminophenoxthionine hydrochloride* [prep. from (**III**) by Br–NaOH etc. or from the Li derivative by NH_2OMe], m.p. 223—225° (decomp.), gives 4-chlorophenoxthionine 10-dioxide, proving the structure of (**II**). 2-Bromophenoxthionine and LiBu^a, followed by CO_2, give 52·3—63·7% (77—89·3% crude) of phenoxthionine-2-carboxylic acid, m.p. 260—265°. 4-Methylphenoxthionine 10-dioxide is stable to boiling, aq. $KMnO_4$–KOH. Dibenzfuran is metallated more readily than is dibenzthiophen by LiBu^a; the Li derivative of the latter metallates the former, but the reverse reaction does not occur. No ring-closure occurs with *o*-OPh·$C_6H_4{\cdot}CO_2H$, S, and $AlCl_3$. 3 : 2 : 1-$NH_2{\cdot}C_6H_3(OPh){\cdot}CO_2H$ (prep. from PhOK and 3 : 2 : 1-$NO_2{\cdot}C_6H_3Br{\cdot}CO_2H$, followed by $SnCl_2$) does not give the sulphinic acid. Attempts to convert (**I**) into dibenzfuran by heating with catalysts failed. CaPhI converts (**I**) into a derivative, which with CO_2 gives phenoxthionine-*x*-carboxylic acid, m.p. 260—262°.

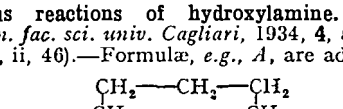
R. S. C.

Preparation of substituted phenylenethiazthionium compounds. M. K. Bezzubetz and V. A. Ignatiuk-Maistrenko (*Prom. Org. Chim.*, 1940, **7**, 377—378).—A 2 : 3 *o*-$C_6H_4Me{\cdot}NH_2,HCl$–S_2Cl_2 mixture, heated at 55°, gives 6-chloro-4-methylphenylenethiazthionium chloride, in 65% yield. 6-Ethoxyphenylenethiazthionium chloride is prepared similarly from *p*-phenetidine.

R. T.

Arylo-thiazolines and -selenazolines.—See B., 1941, II, 6.

Anomalous reactions of hydroxylamine. P. Dreyfuss (*Rend. semin. fac. sci. univ. Cagliari*, 1934, **4**, 55—58; *Chem. Zentr.*, 1935, ii, 46).—Formulæ, *e.g.*, *A*, are advanced for the



(*A.*)

products of interaction of NH_2OH with dibenzylidene*cyclo*hexanone (A., 1934, 773) and 4 : 5 : 4' : 5'-tetramethoxy-2 : 2'-dibenzoylbenzophenone (Vorländer and Gärtner, A., 1899, i, 259).

Ch. Abs. (*c*)

Cyanine dyes.—See B., 1941, II, 7, 8, and 27.

Δ^{α}-Norlupinene. K. Tsuda and J. Yokoyama (*J. Pharm. Soc. Japan*, 1936, **56**, 355—356).—The importance in alkaloid chemistry (*e.g.*, δ-coniceine, matrinidine) of reactions such as the ring-opening of Δ^{α}-picoline and its derivatives and further hydration and acetylation is emphasised. The reaction of α-norlupinine with MeMgI (A., 1936, 212) is paralleled by that of norlupenine. p-*Nitrobenzoyl*-Δ^{α}-1 : 3-*dimethylnorlupinene*, m.p. 95° (prep. described), is a δ-aminoketone (*semicarbazone*, m.p. 173°). CH. ABS. (*c*)

Aconite alkaloids. III. Oxidation of aconitine and derivatives with nitric acid and chromic acid. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1940, **136**, 323—334; cf. A., 1939, II, 350).—Oxidation (HNO_3, *d* 1·42 or 1·2, at 100°) of aconitine (**I**), oxonitine (**II**), ketoaconitine (**III**), or aconitoline (**IV**) yields the neutral nitronitroso-derivative (**V**), $C_{28}H_{26}O_{10}N_3(OMe)_3$ (Suginome, A., 1938, II, 74; Lawson, A., 1936, 351). (**II**) and (**III**) with HNO_3 (*d* 1·42) at 25° give intermediate NO_2-derivatives, respectively $C_{32}H_{36}O_{13}N_2$ (or possibly $C_{33}H_{38}O_{13}N_2$), m.p. 288—289° (decomp. with previous darkening and sintering), converted by HNO_3 at 80° into (**V**), and $C_{33}H_{36}O_{13}N_2$, m.p. 180—190° to a resin, neither of which gives the Liebermann reaction. (**V**) is not affected by 4% MeOH–HCl at 100°, but with MeOH saturated at 0° with HCl, at 25°, yields a sec. *base*, $C_{31}H_{36}O_{12}N_2$, m.p. 252—253° (softening >245°) (cf. Lawson, *loc. cit.*), which reverts to (**V**) with HNO_2. (**I**) with HNO_2 gives a *NO*-derivative, $C_{34}H_{44}O_{13}N_2$, m.p. 281° (cf. Lawson, *loc. cit.*), which with HNO_3 (*d* 1·42) at 25° yields (**V**). (**IV**), proposed formula $C_{33}H_{41}O_{10}N$, which does not react with MeI, is hydrolysed (aq. EtOH–NaOEt) to a base, $C_{24}H_{35}O_8N$ (methiodide, m.p. 222—225°), identical with that obtained by oxidising aconine (Schulze, A., 1908, i, 560). A. LI.

Delphinine. III. Action of hydrochloric, nitric, and nitrons acids on delphinine and its derivatives. W. A. Jacobs and L. C. Craig (*J. Biol. Chem.*, 1940, **136**, 303—321).—Delphinine (**I**) is not affected by 3·3% MeOH–HCl at 100° or by MeOH saturated at 0° with HCl, at room temp., but with MeOH at 100° loses AcOH giving *methylbenzoyldelphonine*, m.p. 173°, $[\alpha]_D^{25}$ +27° in 95% EtOH, oxidised ($KMnO_4$ in $COMe_2$) to methylbenzoyl-α-ketodelphonine (**II**), m.p. 221—223°, resolidifying and remelting at 236—237°, $[\alpha]_D^{25}$ −41·5° in MeOH. α-Ketodelphinine with HNO_3 (*d* 1·42) at 20—25° yields a *substance*, $C_{32}H_{41}O_{10}N$, m.p. 271—273° (decomp.), is not affected by MeOH at 130—140°, but with hot 3% MeOH–HCl (cf. A., 1939, II, 190, 350) yields (**II**) and an amorphous neutral *NO*-derivative, $C_{32}H_{42}O_{10}N_2$, m.p. 228—230°, and with MeOH saturated at 0° with HCl, at 25°, gives first a *Cl*-, $C_{32}H_{40}O_9NCl$, m.p. 242—243° (efferv.), $[\alpha]_D^{25}$ −60° in $CHCl_3$, and finally a Cl_2-derivative, $C_{32}H_{39}O_8NCl_2$ (?), m.p. 225—227° (efferv., previous sintering). The former yields with H_2–PtO_2 at 3 atm. pressure a *hexahydrobenzoyl* derivative, $C_{32}H_{46}O_9NCl$, m.p. 229° (efferv.), and with MeOH at 100°, a mixture containing a neutral substance, $C_{32}H_{39}O_9N$ (?), m.p. 282—284° (decomp.), and a base, $C_{32}H_{39}O_9N$, m.p. 218—220° (previous sintering) [NO-derivative, m.p. 236—238° (previous sintering)]. β-Ketodelphinine is not affected by HNO_3 (*d* 1·42) at 25°, or by MeOH saturated at 0° with HCl, at room temp., but with 4% MeOH–HCl at 100° yields *methylbenzoyl-β-ketodelphonine*, m.p. 182—185° (not sharp), $[\alpha]_D^{30}$ +27° in MeOH, unaffected by saturated MeOH–HCl at room temp. Pyro-α-ketodelphinine (**III**) yields, with aq. HCl (*d* 1·19), a *chloro*-, $C_{30}H_{36}O_7NCl$ (**IV**), m.p. 318—320° (previous darkening), and with MeOH saturated at 0° with HCl, at 20—25°, a Cl_2-derivative, $C_{29}H_{33}O_6NCl_2$ (discolours at >240°, sinters at 260—265°), which when boiled with MeOH yields the substance, $C_{31}H_{39}O_8N$, obtained (*loc. cit.*) by heating (**III**) with MeOH–HCl, and when hydrogenated (PtO_2) gives a H_6-derivative, m.p. 216—218°. (**III**) with HNO_3 (*d* 1·42) at 20° yields a *demethyl*, $C_{36}H_{37}O_8N$, m.p. 309—310°, converted by aq. HCl (*d* 1·19) into a *Cl*-derivative, $C_{30}H_{36}O_7NCl$ (sinters >242°, loses transparency >272°), different from (**IV**). (**III**) with HNO_3 (*d* 1·42) at 50° loses another OMe giving a *product*, $C_{28}H_{33}O_8N$ (?), m.p. 235—240° (sintering >200°). (**I**) with HNO_2 at 100° yields a *NO*-derivative, $C_{33}H_{44}O_{10}N_2$ [(N)Me 0·55%], m.p. 240—241° (decomp., previous sintering), and (chiefly) *hydroxydelphinine*, m.p. 180—182° (efferv.) (occasionally 193—195°), $[\alpha]_D^{20}$ +7° in EtOH, oxidised ($KMnO_4$ in $COMe_2$) to *γ-ketodelphinine*, m.p. 226—229°, $[\alpha]_D^{20}$ +40° in AcOH, which with 4·3% MeOH–HCl at 100° yields *methylbenzoyl-γ-ketodelphonine*, m.p. 184—188° (sinters at >140°), $[\alpha]_D^{30}$ +5° in MeOH. Both *benzoyldelphinine* (BzCl in C_5H_5N), m.p. 171—173°, and its oxidation product ($KMnO_4$ in $COMe_2$), *benzoylketodelphinine*, m.p. 185—187°, lose AcOH on heating. The significance of these results is discussed. A. LI.

Aminoanabasines. V. Aminomethylanabasines and their acyl derivatives. M. I. Kabatschnik and A. I. Zitzer (*J. Gen. Chem. Russ.*, 1940, **10**, 1007—1012).—*N*-Methylanabasine and $NaNH_2$ in $NPhMe_2$ (18 hr. at 120—150°) yield a mixture of 2-[2-N-*Ac*, m.p. 72—73°, and -Ac_2 derivative, b.p. 160—162°/4 mm. (+H_2O, m.p. 60·5—62·5°)], and 5-amino-3-(2'-*N*-methylpiperidyl)pyridine, m.p. 91·5—92·3° [*picrate*, m.p. 227·5—228° (decomp.); 5-N-*Ac*, m.p. 122—122·5°; 5-N-*propionyl*, m.p. 97—98°; 5-N-*Bz*, m.p. 104—106°; 5-N-Bz_2 derivative, m.p. 142—143°]. The toxicity and pharmacodynamic activity of the acylamino- is < that of aminomethylanabasines. R. T.

VII.—PROTEINS.

Molecular structure of myosin. W. T. Astbury and S. Dickinson (*Proc. Roy. Soc.*, 1940, **B**, **129**, 307—332; cf. Woods, A., 1938, I, 347).—A method of preparing films of myosin for *X*-ray and elasticity experiments and methods of orienting myosin chain-mols. are described. The α-photograph of oriented unstretched myosin is almost indistinguishable from that of unstretched keratin, and the β-photograph of stretched myosin is almost indistinguishable from that of stretched keratin, long-range elasticity in both substances depending on reversible intramol. transformation, and the fully extended β-form of the mol. being approx. twice as long as the folded α-form. The resemblance is not between myosin and normal keratin but between myosin and the labile supercontracting form of keratin in which cross-linkings (including S·S bridges) of the polypeptide grid are broken, and the selective orientation produced in moist myosin at room temp. is analogous to that produced in keratin only at higher temp. Similarly, myosin supercontracts in hot H_2O or cold dil. alkali without the preliminary stretching required by keratin. Supercontraction in myosin is due to disorientation of long thin units and, in addition, to folding of the polypeptide chain. An interpretation of the denaturation of myosin is given and it is suggested that the contraction of muscle depends on the supercontraction of its myosin. W. McC.

VIII.—ANALYSIS.

Apparatus for semi-microdetermination of carbon and hydrogen. C. Niemann and V. Danford (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 563—566).—The construction and operation of a furnace for the determination of C and H on 15—30-mg. samples are described in great detail. The normal Pregl combustion train is employed. J. D. R.

Micro-technique of organic qualitative analysis. Group tests for compounds of carbon, hydrogen, and oxygen. D. G. Foulke and F. Schneider (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 554—556).—Methods and procedure are outlined for carrying out the following tests: Fehling's test, osazone formation, the AcCl and $ZnCl_2$–HCl tests for alcohols, Br addition test for phenols, the phthalein fusion test for phenols (all carried out in capillary tubes), the $NaHSO_3$ test for ketones, the CHI_3 test, and the $AlCl_3$ test. Methods for determining *d* and solubility are indicated and detailed procedure is given for oxidation of side-chains and determination of sap. vals. on small quantities of material. J. D. R.

Determination of hydroxyl groups with Grignard reagent. W. Fuchs, N. H. Ishler, and A. G. Sandhoff (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 507—509).—A special apparatus designed for the determination of active H by the Zerevitinov method is described. It is specially suitable for occasional determinations and is simpler in design and operation than that of Kohler. The Grignard reagent is prepared in Bu^{α}_2O. J. D. R.

Effect of carbonyl derivatives as impurities in alcohols. B. J. Fontana and T. D. Stewart (*J. Amer. Chem. Soc.*, 1940, **62**, 2878—2879).—Dissociation of OH·CMe_2·CN in nine different alcohols has been studied. A method for estimating carbonyl impurities by calculation from their effects on the dissociation is outlined. W. R. A.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MARCH, 1941.

I.—ALIPHATIC.

Ozonisation of organic compounds. C. C. Spencer, W. I. Weaver, E. A. Oberright, H. J. Sykes, A. L. Barney, and A. L. Elder (*J. Org. Chem.*, 1940, **5**, 610—617).—Vapour-phase ozonisation of org. compounds proceeds more rapidly than ozonisation in solution owing to the greater concn. of the reactants but is applicable only to compounds with appreciable v.p. and those forming stable ozonides. The chief difficulty is caused by the ozonide mists not being easily wetted by solvents. To overcome this an electrical precipitator (described) is used. Dipentene as vapour gives a diozonide whereas in heptane a mono-ozonide is produced. Under like conditions *d*-limonene gives a di- and a mono-ozonide. Citral, ionone, *ψ*-ionone, citronellol, citronellal, terpineol, carvone, geraniol, and *iso*eugenol are not sufficiently volatile to produce appreciable amounts of ozonide. Ozonisation of pinene as vapour results in oxidation of CH_2 in the *α*-position to the double linking as well as in the addition of O_2 to the unsaturated linking. Complete ozonisation of $(CH_2{:}CH)_2$ (I) in $CHCl_3$ gives an *αβ*–*γδ* diozonide sol. in $CHCl_3$ which cannot be readily isolated owing to its great explosiveness. $H_2C_2O_4$ separates when its solution in $CHCl_3$ is kept. Hydrolysis effected in the presence of $CHCl_3$ gives CH_2O and glyoxal. *Δ$^{\alpha\gamma}$-Butadiene mono-ozonide* (II) results when O_3 is passed through (I) in light petroleum. The products of its hydrolysis do not appear to contain maleic anhydride as judged by attempts at its isolation through the 2 : 4-dinitrophenylhydrazone or by conversion into maleic acid. Hydrolysis yields CH_2O and acraldehyde, indicating *αγ* addition. Evidence of *αδ* addition could not be found. (II) is relatively stable. H. W.

Hydrogenation of oxygen-containing compounds. III. Preparation of *βγ*-dimethylbutane from pinacolin. B. Moldavski and T. Nizovkina (*J. Gen. Chem. Russ.*, 1940, **10**, 653—654).—Pr^{β}_2 is obtained in 65% yield by hydrogenation of COMeBu$^{\gamma}$ (MoS_2 catalyst; 4 hr. at 340—350°). R. T.

Isomerisation of *n*-heptane and *n*-octane. A. P. Sivertzev (*J. Gen. Chem. Russ.*, 1940, **10**, 799—802).—*iso*-Octane or -heptane is obtained in ~10% yield when the *n*-hydrocarbons are passed through a porcelain tube at 450—600°. With 10% of $AlCl_3$ at 50—60° the yield is 31—37%. R. T.

Application of the xanthate method of L. A. Tschugaev to dihydric alcohols or their corresponding dibromides. V. E. Tischtschenko, V. N. Schabaschova, and N. D. Sisoeva (*J. Gen. Chem. Russ.*, 1940, **10**, 1042—1054).—$OEt{\cdot}CS_2Na$ (I) and *sec.-tert.*- or di-*tert.*-dibromides at 60—80° react as follows: $C_nH_{2n}Br_2 + 2(I) \rightarrow C_nH_{2n}(CS_2{\cdot}OEt)_2$ (II) $+2NaBr$; (II) $\rightarrow C_nH_{2n} + (OEt{\cdot}CS_2)_2$ (III); (III) $\rightarrow CS(OEt)_2 + COS + S$. The hydrocarbon so obtained from $CH_2Br{\cdot}CMe_2Br$ is $(CMe{:})_2$, and from $CHMeBr{\cdot}CMe_2Br$ is $CHMe{:}CMe_2$. $SK{\cdot}CO_2Et$ reacts similarly to (I), the products being C_nH_{2n}, KBr, and $(S{\cdot}CO_2Et)_2$. R. T.

αα-Dichlorides of the allene series. Action of phosphorus pentachloride on methyl vinyl ketone. A. N. Tschurbakov (*J. Gen. Chem. Russ.*, 1940, **10**, 977—980).—$CH_2{:}CHAc$ (I) and PCl_5 at 0° yield $CH_2Cl{\cdot}CH{:}CMeCl$, converted by 15% Na_2CO_3 at 100° into (I) and $OH{\cdot}CH_2{\cdot}CH{:}CMeCl$ (*phenylurethane*, m.p. 78·8°), which with 16% H_2SO_4 (3 hr. at 100°) also gives (I). R. T.

Manufacture of dihalogenobutanes.—See B., 1941, II, 32.

Preparing ethyl alcohol from ethylene of petroleum gases.—See B., 1941, II, 30.

Conjugated systems. X. Reaction of bromoprene with hypobromous acid. A. A. Petrov (*J. Gen. Chem. Russ.*, 1940, **10**, 1013—1020).—Bromoprene (I) and HOBr (from NHAcBr) yield *αγ-dibromo-Δ$^{\gamma}$-buten-β-ol*, b.p. 91—92·5°/10 mm. (*acetate*, b.p. 99·5—100·5°), which with Br in $CHCl_3$ gives *αββδ-tetrabromobutan-γ-ol*, m.p. 61·5—63°. This is oxidised ($Na_2Cr_2O_7$ in H_2SO_4) to *αββδ-tetrabromobutan-γ-one*, b.p. 151—153°/10 mm. (I) at 150° with 60% aq. KOH yields *bromoprene oxide* (II), b.p. 130·5—131°, converted by 1% H_2SO_4 (3 hr. at 40°) into *β-bromo-Δ$^{\alpha}$-butene-γδ-diol*, b.p. 120—121°/10 mm. (*di-acetate*, b.p. 116—117°/10 mm.). With Br in $CHCl_3$ (II) gives *αββ-tribromobutane-γδ-diol*, m.p. 121·5—123°, whilst with HBr at −5° (II) affords *βγ-dibromo-Δ$^{\alpha}$-buten-δ-ol*, b.p. 99·5—101°/10 mm. (*acetate*, b.p. 108—109°/10 mm.). R. T.

Grignard synthesis of unsaturated halogeno-alcohols. G. I. Schtukin (*Bull. Sci. Univ. Kiev*, 1939, No. 4, 45—80).—$CH_2{:}CH{\cdot}CH_2{\cdot}MgBr$ and $COMe{\cdot}CH_2Cl$ or $CO(CH_2Cl)_2$ in Et_2O yield *α-chloro-β-methyl-* (I), b.p. 53°/10 mm., 159°/750 mm., or *α-chloro-β-chloromethyl-Δ$^{\delta}$-pentcn-β-ol* (II), b.p. 82·5°/14 mm., 190°/750 mm. (decomp.). With $NHEt_2$ or KCN (I) affords *α-diethylamino-*, b.p. 158—160°/750 mm., or *α-cyano-β-methyl-Δ$^{\delta}$-penten-β-ol*, b.p. 112°/17 mm.; the corresponding products from (II) were oils, decomp. at the b.p. R. T.

Reaction of *ββ′*-dichlorodiethyl ether with dimagnesium dibromoacetylene. S. N. Popov (*J. Gen. Chem. Russ.*, 1940, **10**, 1141—1143).—$(Cl{\cdot}[CH_2]_2)_2O$ is converted into $(Br{\cdot}[CH_2]_2)O$ by the action of $(C{:}C{\cdot}MgBr)_2$ in Et_2O. R. T.

Conjugated systems. IX. Reactions of β-halogenobutadienes with alkyl hypoiodites, and the synthesis of halogeno-alkoxyprenes. A. A. Petrov (*J. Gen. Chem. Russ.*, 1940, **10**, 819—825).—The ethers $CH_2{:}CX{\cdot}CH(OR){\cdot}CH_2I$ (X = Cl, R = *Me*, b.p. 76·5—77°/10 mm., R = *Et*, b.p. 82—83°/10 mm.; X = Br, R = *Me*, b.p. 91·5—92°/10 mm., R = *Et*, b.p. 97·8°/10 mm.) are prepared from chloro- or bromo-prene, ROH, HgO, and I at room temp. With NaOH–EtOH the ethers yield $CH_2{:}CX{\cdot}C(OR){:}CH_2$, whilst with dil. H_2SO_4 the ketones $COMe{\cdot}CX{:}CH_2$ are obtained. R. T.

Structure of kephalin. E. Le B. Gray (*J. Biol. Chem.*, 1940, **136**, 167—175).—The isolation of kephalin (I) from brain, liver, and heart by a modification of Bloor's method (A., 1926, 752) is described. Reduction of (I) in AcOH–*cyclo*hexane (1 : 1) (PtO_2–H_2) gives a non-hygroscopic amorphous product, m.p. 156—162°, which differs from unreduced (I) only in those properties which depend on degree of unsaturation. Discrepancies between the theoretical and observed composition of (I) are due to the presence of a hitherto unidentified group or groups low in C and H and high in O. Cuorin is not produced during extraction of lipins but exists preformed in heart and liver (not brain). W. McC.

Manufacture of α-chloroacrylic acid esters.—See B., 1941, II, 33.

Synthesis of alkyl ethylene orthoformates. V. G. Mchitarian (*J. Gen. Chem. Russ.*, 1940, **10**, 667—669).—$(CH_2{\cdot}OH)_2$ and $CH(OEt)_3$ in presence of p-$C_6H_4Me{\cdot}SO_3H$ (I) (10 min. at the b.p.) yield *ethylene Et orthoformate*, $\begin{matrix}CH_2{\cdot}O\\CH_2{\cdot}O\end{matrix}\!>\!CH{\cdot}OEt$, b.p. 120—123°. With menthol or borneol and (I) (2 hr. at the b.p.) this gives *menthyl*, m.p. 34·2°, or *bornyl ethylene orthoformate*, b.p. 148—152°/16 mm. R. T.

Production of lævulic acid.—See B., 1941, II, 33.

Vitamin-*C* available from plant sources in Taiwan. IV. Reaction between ascorbic acid and magnesium oxide. R.

Yamato and T. Hara (*J. Agric. Chem. Soc. Japan*, 1940, **16**, 1038—1040; cf. A., 1940, III, 751).—Ascorbic acid (I) and 0·5 mol. of MgO in H_2O give the *salt* $(C_6H_7O_6)_2Mg$, $[\alpha]_D^{19}$ +96·5°. With 40 mols. of MgO an insol. substance is formed which yields (I) when treated with acid. J. N. A.

Improved preparation of *d*-galacturonic acid. W. W. Pigman (*J. Res. Nat. Bur. Stand.*, 1940, **25**, 301—303; cf. Mottern and Cole, A., 1940, III, 72).—Citrous polygalacturonide in aq. NaOH (p_H 3·7) is incubated (38°) with pectinase for 10—14 days, neutralised (H_2SO_4), and filtered. The filtrate when evaporated to a syrup and extracted with boiling MeOH gives galacturonic acid monohydrate, m.p. 109—112°, $[\alpha]_D^{20}$ +51·5°, in 74% yield. J. L. D.

Lipins of tubercle bacilli. LXII. Mycolic acid. A. Lesuk and R. J. Anderson (*J. Biol. Chem.*, 1940, **136**, 603—613; cf. A., 1939, II, 48).—Mycolic acid (I) with PhOH, Ac_2O, and HI (*d* 1·73) at 150° yields iodohydroxy-, reduced (Zn + AcOH–C_5H_{11}·OH) to *hydroxy-normycolic acid*, m.p. 56—58°, and a *OH-acid*, $C_{104}H_{208}O_3$ (?), m.p. 74—76°, $[\alpha]_D^{25}$ +4·03° in $CHCl_3$ (*Me* ester, m.p. 63—65°), both of which yield *n*-$C_{25}H_{51}$·CO_2H (II) at 250—300° (reduced pressure). With PhOH, Ac_2O, and HI (*d* 1·86) at 150° (I) yields *di-iodo-normycolic acid*, m.p. 41—43°, reduced to *normycolic acid*, $C_{87}H_{174}O_2$, m.p. 52—54° (Me ester), which gives no volatile acid when heated. Oxidation (CrO_3 in glacial AcOH) of (I) yields a mixture containing *n*-$C_{17}H_{35}$·CO_2H, (II), and *n*-CO_2H·$[CH_2]_{16}$·CO_2H. It is concluded that (I) is a mixture of two acids, the principal one having two *n*-C_{26} chains with CO_2H on one. A. Li.

***α-tert.*-Butylsulphonylpropionic acid and its mono-bromo-derivative.** B. Bäcklund (*Arkiv Kemi, Min., Geol.*, 1940, **14**, A, No. 1, 25 pp.).—*α*-tert.-*Butylthiolpropionic acid*, m.p. 92° (corr.), from BuᵞOH and SH·CHMe·CO_2H in aq. HCl, gives with neutral $KMnO_4$ *α*-tert.-*butylsulphonylpropionic acid* (I), m.p. 139° (corr.). The bromination of (I) in N-HBr has been studied from 35° to 100°; 2 mols. of Br are rapidly absorbed with hydrolysis, giving BuᵞOH and SO_2H·CBrMe·CO_2H. Further absorption of Br (changes of rate at 3 and 5 mols. of Br) is due to bromination of BuᵞOH. In buffered solutions (initial p_H 3·5, final 1·7) 1 mol. of Br is added (at 35°) to give the *α-Br*-derivative (II), m.p. 83° (decomp.), which gives I with acid KI. (II) decomposes slowly at room temp., rapidly at 100°, giving SO_2 0·80, CMe_2:CH_2 0·25, tri*iso*butene 0·27, and CHMeBr·CO_2H (III) 0·72 mol. Hydrolysis of (II) by N-HBr at 35° gives BuᵞOH, (I), (III), SO_2, HBr, and H_2SO_4. M. H. M. A.

Production of formaldehyde by means of the electric arc at high and low frequencies.—See A., 1941, I, 86.

Accelerating effect of ketones on the Cannizzaro-Tischtschenko reaction. III. Action of ββ-dihydroxymethylbutan-γ-one. M. N. Tilitschenko (*J. Gen. Chem. Russ.*, 1940, **10**, 718—722; cf. A., 1939, II, 49).—$CMeAc(CH_2·OH)_2$ is a more active catalyst of the Cannizzaro reaction than is COMeEt. R. T.

Electrolytic reduction potentials of organic compounds. XXVIII. Determination of sugars by polarographic method. Determination of pentoses and pentosan. I. Tachi (*J. Agric. Chem. Soc. Japan*, 1940, **16**, 1057—1063; cf. A., 1939, I, 84).—Pentoses and pentosan are hydrolysed to furfuraldehyde (I), which is determined by the polarographic method. The relation between concn. and height of the reduction curve of (I) is very important, and when the height is determined by the so-called tangent point method, there is a linear relation. (I) is quantitatively formed when xylose is heated with HCl (*d* 1·06) at 160° for 2—3 hr. J. N. A.

Lecture experiment for distinguishing fructose from glucose [sucrose, lactose, or maltose]. E. W. Zmaczynski (*J. Chem. Educ.*, 1940, **17**, 399—400).—1—2 drops of aq. $Pb(OAc)_2$ and 1—2 c.c. of glycerol are added to 60—100 mg. of the sugar mixed with 10—15 mg. of S. With fructose, a black colour is obtained on heating. L. S. T.

Starch. VIII. Degradation of the constituents of starch by β-amylase. K. H. Meyer, P. Bernfeld, and J. Press (*Helv. Chim. Acta*, 1940, **23**, 1465—1476; cf. A., 1940, II, 336).—Oxidation of the aldehydic functions of starch by I followed by removal of excess of halogen leaves a residue which is normally degraded by β-amylase (I). They are therefore not concerned in the degradation by (I) which attacks the glucose residues with free OH at $C_{(2)}$, $C_{(3)}$, $C_{(4)}$, and $C_{(6)}$. The so-called "enzymic coagulation" of amylose (II) is connected with the greater solubility of crude (II) in comparison with (II) of higher mol. wt. obtained by fractionation. The portions of lower mol. wt. act as protective colloids to those of higher mol. wt., and these are the portions which are preferentially attacked by (I). Incomplete degradation of (II) by (I) may be due to contamination of (II) with amylopectin (III), in which case the residual solution gives a red to violet colour with I or pure (II) may become aged during enzymic attack and a pure blue colour is then obtained with I. Provided that agency is eliminated, the graph for the degradation of (II) by (I) is rectilinear until 65% hydrolysis has occurred. This is explained by assuming the removal of a maltose residue from the end of the chain whereby a second similar group is uncovered so that the concn. of terminal groups and enzyme is const. Only when degradation verges towards complete hydrolysis of some chains is there a diminution of the no. of terminal groups with consequent deceleration of the reaction. Degradation of (III) by (I) is invariably accompanied by the production of a residual substance of high mol. wt. and is not suited to kinetic study. It is conveniently replaced by starch degraded in glycerol, with which the reaction is of zero order only until 30—40% degradation has occurred; subsequently the rate diminishes rapidly partly because fewer terminal groups are available owing to variation in the length of the chains and partly owing to branching of the chains. Fresh solutions of pure (II) are degraded more slowly than those of sol. starch consisting essentially of (III) since the latter has the larger no. of terminal groups. H. W.

***X*-Ray comparison of natural and synthetic starch.** W. T. Astbury and C. S. Hanes (*Nature*, 1940, **146**, 558).—Purified potato starch and the polysaccharide synthesised by the action of potato phosphorylase on glucose 1-phosphate give essentially the same *X*-ray powder pattern (reproduced), with that of the synthetic starch not quite so sharp. Amyloamylose pptd. by EtOH after electrophoretic separation gives a *V*-pattern photograph, whilst the synthetic starch after pptn. by EtOH gives the *B*-pattern. L. S. T.

Manufacture of dimethylamine.—See B., 1941, II, 33.

Production of amino-acids.—See B., 1941, II, 34.

Reaction of formaldehyde with amino-acids. *X*-Ray diffraction patterns. A. K. Smith, P. Handler, and J. N. Mrgudich (*J. Physical Chem.*, 1940, **44**, 874—880).—*X*-Ray diffraction patterns of CH_2O-treated histidine (I) show that the product is cryst. Arginine and lysine similarly treated give amorphous products. The free bases are cryst. in each case. The cryst. nature of the CH_2O–(I) product is increased by ageing. The other two products are unchanged after several months' ageing. C. R. H.

Identification of primary aliphatic amides as oxalates. C. A. Mackenzie and W. T. Rawles (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 737—738).—By heating the appropriate amide and $H_2C_2O_4$ in EtOAc the following *compounds* are formed: $(HCO·NH_2)_2,H_2C_2O_4$, m.p. 107·4—107·7°, $NH_2Ac,H_2C_2O_4$, m.p. 127·3°, $EtCO·NH_2,H_2C_2O_4$, m.p. 80·8—81·0°, $(PrCO·NH_2)_2,H_2C_2O_4$, m.p. 65·9—66·2°, $(BuCO·NH_2)_2,H_2C_2O_4$, m.p. 61·1—61·4°, $(C_5H_{11}·CO·NH_2)_2,H_2C_2O_4$, m.p. 71·1—71·3°. Interaction of amides and $H_2C_2O_4$ in H_2O yields only $(NH_4)HC_2O_4,H_2C_2O_4$, and $Pr^βCO·NH_2$ failed to yield a salt. J. D. R.

Preparation of nitriles.—See B., 1941, II, 34.

Reaction of magnesium *tert.*-butyl chloride with propionyl, *iso*butylacetyl, and benzoyl chloride. A. D. Petrov and N. A. Roslova (*J. Gen. Chem. Russ.*, 1940, **10**, 973—976).—EtCOCl and MgBuᵞCl in Et_2O yield $COEt_2$, COEtBuᵞ, $Pr^αOH$, $EtCO_2H$, $EtCO_2CHEt_2$, and $EtCO_2CHEtBu^γ$. With $CH_2Bu^β·COCl$ the products are iso*hexyl* iso*butylacetate*, b.p. 170—178°, and di*iso*amyl ketone, reduced by Kishner's method to *ββ-dimethylnonane*, b.p. 177—178°. BzCl does not react with MgBuᵞCl at room temp., whilst in boiling xylene only tarry products are obtained. R. T.

Metallo-organic compounds. IX. Tristrimethyltin oxonium halides, $[SnMe_3]_3OX$. T. Harada (*Bull. Chem. Soc. Japan*, 1940, **15**, 455—458).—The oxonium *compounds* $(SnMe_3)_3OI$, m.p. 94°, and $(SnMe_3)_3OBr$, m.p. 88°, have been obtained by the action of $(SnMe_3)_2O$ on $SnMe_3I$ or $SnMe_3Br$ in an anhyd. solvent. F. J. G.

II.—HOMOCYCLIC.

Products of the oxidation of 1 : 1 : 4-trimethylcycloheptene. H. Barbier (*Helv. Chim. Acta*, 1940, **23**, 1477—1480; cf. A., 1940, II, 217).—Re-examination of the product of the oxidation of trimethylcycloheptene by SeO_2 confirms the formation of 2 : 5 : 5-trimethyl-Δ^2-*cyclo*heptenone (**I**) and reveals the presence of 4 : 4-*dimethyl*-Δ^1-cyclo*hepten*-1-*aldehyde*, b.p. 76°/4 mm. The semicarbazone, m.p. 195—196° (*loc. cit.*), is separated into two portions, m.p. 177° [hydrolysed to (**I**)] and m.p. ~196—200°. The last-named, when hydrolysed and oxidised by Ag_2O, gives 4 : 4-*dimethyl*-Δ^1-cyclo*heptene*-1-*carboxylic acid*, m.p. 63—64° (p-*phenylphenacyl* ester, m.p. 73°). H. W.

Photochemical oxidation of aromatic hydrocarbons. A. A. Krasnovski (*J. Gen. Chem. Russ.*, 1940, **10**, 1094—1100).—A colorimetric method of determination of org. peroxides, depending on oxidation of Fe^{II} to Fe^{III} in presence of CNS', is described. Oxidation of PhMe by atm. O_2 in ultra-violet light consists of two stages: $PhMe + O_2 \rightarrow PhMe_2O_2 \rightarrow PhCHO + H_2O$. With free access of O_2 the former reaction is of the zero order, and the latter of the first order. R. T.

Alkylation of aromatic hydrocarbons by means of dihalides. I. Condensation of αγ-chlorobromopropane with benzene. I. Tzukervanik and K. Jatzimirski (*J. Gen. Chem. Russ.*, 1940, **10**, 1075—1076).—C_6H_6 and $Cl\cdot[CH_2]_3\cdot Br$ at 12—13° in presence of $AlCl_3$ give chiefly $Br\cdot[CH_2]_3\cdot Ph$ (40%), with PhPr and $Ph\cdot[CH_2]_3\cdot Ph$ (**I**) as by-products. At 80—85° the chief product is (**I**) (60%), with PhPr as a by-product. R. T.

Addition of hydrogen bromide to cholesteryl bromide and the oxygen effect. Y. Urushibara, K. Nambu, and T. Ando (*Bull. Chem. Soc. Japan*, 1940, **15**, 442—448; cf. Mauthner, A., 1907, i, 921).—Cholesteryl bromide (**I**) with HBr and a trace of pyrocatechol or $FeCl_3,6H_2O$ in CCl_4, or with HBr in Et_2O, yields 3 : 5-*dibromocholestane*, m.p. 101·5° (corr.), $[\alpha]_D^{25}$ +5·36° in $CHCl_3$, which when heated in $COMe_2$ gives (**I**), and in C_5H_5N gives $\Delta^{3:5}$-cholestadiene. (**I**) with HBr and O_2 in CCl_4 yields 3 : 6-*dibromocholestane* (**II**), m.p. 154° (corr.), $[\alpha]_D^{25}$ −12·1° in $CHCl_3$, and a compound, $C_{27}H_{45}Br_3$, m.p. (impure) 84—127°, debrominated (NaI in EtOH) to (**I**). (**II**) yields with KOAc in glacial AcOH, cholesteryl acetate, and with Na + C_5H_{11}·OH, cholestene. A. Li.

Reduction of nitro-compounds by means of sodium sulphide. S. Raschevskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 1089—1093).—Reduction is effected via the stages: $4Na_2S + R\cdot NO_2 + 4H_2O \rightarrow NH_2R + Na_2S_4 + 6NaOH$ (at 50°); $3Na_2S_4 + 5R\cdot NO_2 + 6NaOH + 2H_2O \rightarrow 5NH_2R + 6Na_2S_2O_3$. R. T.

Substituted amides. C. V. Bowen and L. E. Smith (*J. Amer. Chem. Soc.*, 1940, **62**, 3522—3523).—The following are prepared. *Propion*-m-4-, m.p. 137—137·5°, -p-, m.p. 138°, and -m-2-*xylidide*, m.p. 115·5—116·5°, and -*xenylamide*, m.p. 176—177°. *Laur*-*benzylamide*, m.p. 82—82·5°, and -m-*toluidide*, m.p. 54—56°. *Palmit*-cyclo*hexylamide*, m.p. 94—95°, -*benzylamide*, m.p. 94·5—95°, -o-, m.p. 90—91°, and -m-*toluidide*, m.p. 74·5—75·5°. 2-*Furo*-cyclo*hexylamide*, m.p. 112—112·5°, -*benzylamide*, m.p. 110·5—111°, -m-4-, m.p. 104—105°, -p-, m.p. 89—90°, and -m-2-*xylidide*, m.p. 125—126°, -α-, m.p. 155—156°, and -β-*naphthylamide*, m.p. 152—153°, -2-*fluorylamide*, m.p. 201—201·5°, and -*xenylamide*, m.p. 171—172°. R. S. C.

Substituted adipanilides.—See B., 1941, II, 35.

Chemotherapeutic compounds of the streptocide series. II. M. V. Rubtzov (*J. Gen. Chem. Russ.*, 1940, **10**, 831—843).—The activity of the following compounds has been compared (figures in parentheses refer to the streptocidal activity, that of streptocide being taken as 100; compounds marked * are toxic): *p*-NHR·C_6H_4·SO_2·NH_2, where R = CH_2Ph (70), *γ-diethylaminopropyl** (45), m.p. 140—142° (*hydrochloride*, m.p. 118—119°), γ-diethylamino-β-hydroxypropyl* (10), m.p. 112°, CH_2·CO_2H (125), m.p. 265—266° (decomp.), CH_2·CO·NH_2 (85), m.p. 203—204°, CH_2·SO_3Na (90), SO_3Na (20), H (80), *p*-NH_2·C_6H_4·SO_2 (30), and *p*-NHAc·C_6H_4·SO_2 (55); *p*-NH_2·C_6H_4·SO_2·NHR, where R is CH_2Ph (65), m.p. 119—119·5° (N-*Ac* derivative, m.p. 160—161°), *p*-NH_2·C_6H_4·SO_2 (33), 4-*amino*-3-*sulphophenyl* (60), *p*-NH_2·C_6H_4 (100) (N-*Ac* derivative, m.p. 228—229°), pp′-NH_2·C_6H_4·SO_2·NH·C_6H_4· (100), m.p. 268—269° (decomp.), pp′-NH_2·C_6H_4·SO_2·NH·$C_6H_3(SO_3H$-*m*$)$ (25). Antipyrine and $ClSO_3H$ (5 hr. at 70—80°) yield *antipyrinesulphonyl chloride*, m.p. 185·5—187°, from which *antipyrinesulphonamide*, m.p. 220—221°, is prepared. R. T.

Isomerism of guanidines. R. P. Sieg and W. M. Dehn (*J. Amer. Chem. Soc.*, 1940, **62**, 3506—3508).—Condensation of NH_2Ar with $C(:NAr')_2$ [prep. *in situ* from $CS(NHAr')_2$ by $Pb(OH)_2$] in C_6H_6 gives only NHAr·C(:NAr')·NHAr′ with small amounts of a carbamide and unchanged starting material. However, NAr′:C:NAr″ gives NHAr·C(:NAr′)·NHAr″ and NHAr·C(:NAr″)·NHAr′. Only one H thus migrates during the condensation. Literature data are corr. The following have been prepared, numbering being N·C(:N″)·N′. NN′-*Diphenyl*-N″-o-, m.p. 93°, -m-, m.p. 101°, and -p-, m.p. 104·5°, NN″-*diphenyl*-N′-o-, m.p. 110·5°, -m-, m.p. 92°, and -p-, m.p. 121°, N″-*phenyl*-NN′-*di*-o-, m.p. 93·5°, -m-, m.p. 92°, and -p-, m.p. 62°, N′-*phenyl*-NN″-*di*-o-, m.p. 97°, -m-, m.p. 86°, and -p-, m.p. 82·5°, NN′-*di*-o-*tolyl*-N″-m-, m.p. 88°, and -p-, m.p. 70·5°, NN″-*di*-o-*tolyl*-N′-m-, m.p. 86°, and -p-, m.p. 83°, NN′-*di*-m-*tolyl*-N″-o-, m.p. 90°, and -p-, m.p. 103°, NN″-*di*-m-*tolyl*-N′-o-, m.p. 84°, and -p-, m.p. 93°, NN′-*di*-p-*tolyl*-N″-o-, m.p. 77·5°, and -m-, m.p. 83·5°, NN″-*di*-p-*tolyl*-N′-o-, m.p. 89·5°, and -m-, m.p. 101°, -*tolylguanidine*. R. S. C.

Chemotherapeutic compounds of the streptocide series. I. Compounds containing the azo-group. O. J. Magidson and M. V. Rubtzov (*J. Gen. Chem. Russ.*, 1940, **10**, 756—768).—The following compounds have been prepared by standard reactions (figures in parentheses refer to streptocidal activity; compounds marked * are toxic): 2 : 4-diaminoazobenzene-4′-sulphonamide hydrochloride [streptocide] (100), N-(p′-2″ : 4″-*diaminobenzeneazobenzenesulphonyl*)*sulphanilamide* (55), m.p. 223—225° (decomp.), 2 : 4-*diaminoazobenzene*-3′-*sulphonamide*, m.p. 198° [*hydrochloride* (50), m.p. 219°], 6-amino-5-benzeneazoquinoline-4′-sulphonamide (100), 4-(γ-*diethylamino*-β-*hydroxypropylamino*)*azobenzene*-4′-*sulphonamide* (100), m.p. 166—167°, 4-(β-*diethylaminoethylamino*)*azobenzene*-4′-*sulphonamide** (90), m.p. 185—186°, α-*anilino*-γ-*diethylamino*-β-*hydroxypropane*, b.p. 189—190°/12 mm., 5-benzeneazo-6-hydroxyquinoline-4′-sulphonamide (100) [hydrochloride, not melting at 290° (lit. m.p. 268°)], 1-*amino*-7-*benzeneazo*-8-*hydroxy*-3 : 6-*disulphonaphthalene*-4′-*sulphonamide** (100) [N-*Ac* derivative (100)], 7-*benzeneazo*-1 : 3 : 6-*trisulphonaphthalene*-4′-*sulphonamide* (40), 2-amino-4-hydroxyazobenzene-4′-sulphonamide (90), 2 : 4-diamino-6-carboxyazobenzene-4′-sulphonamide* (85), 2 : 4-dihydroxyazobenzene-4′-sulphonamide* (100), 7-*benzeneazo*-1 : 8-*dihydroxy*-3 : 6-*disulphonaphthalene*-4′-*sulphonamide* (80), and 4-*amino*- (50), m.p. 225—228°, and 4-*hydroxy*-3-*carboxyazobenzene*-4′-*sulphonamide* (100). R. T.

Diazo-compounds. II. Reaction of diazo-compounds with complex heteropoly-acids. V. V. Kozlov and B. N. Archipov. **III. Complex diazo-compounds of phenylenediamines with heteropoly-acids, and certain dyes produced therefrom.** V. V. Kozlov, B. N. Archipov, and A. V. Simonovskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 685—696, 697—704).—**II.** The *salts* $(RN_2)_3H_4P(M_2O_7)_6$, where M is Mo or W, and $(RN_2)_4H_4Si(W_2O_7)_6$ (R = Ph, *o*- and *p*-NO_2·C_6H_4·, *p*-C_6H_4Me·, and *o*-OMe·C_6H_4·), were prepared from aq. RN_2Cl and the appropriate acids, or by diazotisation of the corresponding salts of the NH_2R. The salts are considerably more stable than are the corresponding halides. In aq. suspension they are decomposed by Cu powder, in the same way as ordinary diazonium salts.

III. The *salts* $[R(NH_2)_2]_3[H_7P(M_2O_7)_6]_2$ where M is Mo or W, and $[R(NH_2)_2]_2H_8Si(W_2O_7)_6$ (R is *m*- and *p*-C_6H_4, and 1 : 5-$C_{10}H_6$) have been prepared. Aq. suspensions of these salts when diazotised yield diazonium salts of the types $[(NH_2\cdot R\cdot N_2)_3H_4P(M_2O_7)_6]\cdot[H_7P(M_2O_7)_6]$ and $(NH_2\cdot R\cdot N_2)_2H_2[H_4Si(W_2O_7)_6]$, and couple with β-$C_{10}H_7$·OH giving the azo-dye salts $(NH_2\cdot R\cdot N_2\cdot C_{10}H_6\cdot OH)_3,H_7P(M_2O_7)_6$ and $(NH_2R\cdot N_2\cdot C_{10}H_6\cdot OH)_4,H_8Si(W_2O_7)_6$, from which the azo-dyes are liberated by aq. NaOH. R. T.

Preparation of alkylphenols.—See B., 1941, II, 36.

Synthesis of amylphenol.—See B., 1941, II, 30.

Oxidation of *p*-propenylphenol derivatives.—See B., 1941, II, 36.

Molecular structure in relation to œstrogenic activity. Derivatives of 4 : 4′-dihydroxydiphenylmethane. N. R. Camp-

bell (*Proc. Roy. Soc.*, 1940, **B**, **129**, 528—538).—The derivatives were prepared from the appropriate CO-compound (1 mol.), PhOH or *o*-cresol (4 mols.), and conc. (at room temp.) or dry HCl (at ~0°). The following are new: *αα-di*-p-*hydroxyphenyl-β-methylpropane*, m.p. 152°, *-γ-methylbutane*, m.p. 145°, *-β-ethylbutane*, m.p. 168°, *-β-n-propylpentane*, m.p. 128°, *-α-phenylpropane*, m.p. 176°, *-β-phenylethane*, m.p. 140°, and *-ββ-diphenylethane*, m.p. 236° (decomp.); *αα-di*-(4-*hydroxy*-3-*methylphenyl*)-*γ-methylbutane*, m.p. 124°; *ββ-di*-(p-*hydroxyphenyl*)-*hexane*, b.p. 210°/0·5 mm., and *-γ-methylpentane*, m.p. 153°; *ββ-di*-(4-*hydroxy*-3-*methylphenyl*)-*pentane*, m.p. 128°, *-hexane*, m.p. 104—105°, and *-γ-methylpentane*, m.p. 128°; *γγ-di*-(p-*hydroxyphenyl*)*hexane*, m.p. 155°; *γγ-di*-(4-*hydroxy*-3-*methylphenyl*)-*pentane*, m.p. 120°, and *-hexane*, m.p. 90°; *δδ-di*-(p-*hydroxyphenyl*)*octane*, m.p. 150°; *δδ-di*-(4-*hydroxy*-3-*methylphenyl*)-*heptane*, m.p. 173°, and *-octane*, m.p. 140°; *εε-di*-(p-*hydroxyphenyl*)*nonane*, m.p. 165°; *εε-di*-(4-*hydroxy*-3-*methylphenyl*)*nonane*, m.p. 128°; 1 : 1-*di*-(p-*hydroxyphenyl*)-2-*methyl*cyclo*hexane*, m.p. 235°, -cyclo*pentane*, m.p. 157°, -2-*methyl*cyclo*pentane*, m.p. 161°, and -3-*methyl*-cyclo*pentane*, m.p. 171°; 1 : 1-*di*-(4-*hydroxy*-3-*methylphenyl*)-cyclo*pentane*, m.p. 162°. The relationship between the determined œstrogenic activity and structure is discussed (A., 1941, III, 100). F. O. H.

Preparation of 2 : 2′-dihydroxydiphenyl.—See B., 1941, II, 36.

Preparation of multivalent iodo-compounds in the *o-*, *m-*, and *p*-iodoanisole series. R. A. Mastropaolo F. (*Anal. Asoc. Quím. Argentina*, 1940, **28**, 101—107).—*o-* and *m*-OMe·$C_6H_4ICl_2$ with aq. 40% NaOH give o- (**I**), m.p. 260—265° (decomp.) (impure), and m-*iodosoanisole*, m.p. 250—251°, respectively; the mother-liquors from (**I**) with KI afford *di*-o-*anisyliodinium tri-iodide*, m.p. 135—136°, converted by H_2O–Ag_2O followed by KI into *di*-o-*anisyliodinium iodide*, m.p. 154° (decomp.). *p*-OMe·C_6H_4·IO, *p*-OMe·C_6H_4·IO_2, and H_2O–Ag_2O followed by KI give *di*-p-*anisyliodinium tri-iodide*, m.p. 145°, whence the *monoiodide*, m.p. 180°. The *m*-iodinium compounds could not be prepared. F. R. G.

2 : 4-Dinitrophenyl alkyl ethers as stimulants of the metabolic rate. L. G. Wesson (*J. Amer. Chem. Soc.*, 1940, **62**, 3466—3468).—2 : 4 : 1-$(NO_2)_2C_6H_3$·OAg (prep. described) and RI at room temp., later 100° (bath), give 2 : 4-*dinitrophenyl* Pr^{α}, m.p. 30·5—31°, b.p. 172—175°/2 mm., Pr^{β} (**I**), m.p. 53·4—53·6°, b.p. 152—156°/0·75 mm. [also obtained from 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$, $Pr^{\beta}OH$, and 80% KOH], Bu^{α}, m.p. 1·5—1·8°, b.p. 178—180°/2 mm., Bu^{β}, m.p. 30·3—31·5°, b.p. 152—154°/1 mm., n-, m.p. 0—1°, b.p. 186—188°/2 mm., and iso-*amyl*, m.p. 9·5—10°, b.p. 175—178°/1 mm., n-*hexyl*, m.p. 4·2—4·6°, b.p. 202—205°/2·5 mm., and n-*heptyl*, m.p. 16·4—16·5°, b.p. 192—194°/1 mm., *ether*. These ethers increase the metabolic rate of rats more slowly than does 2 : 4 : 1-$(NO_2)_2C_6H_3$·OH (**II**). (**I**) causes evolution of only a little NH_3 due to liver damage. 70 mg. per kg. body-wt. fed to rats for 1 month increased the basal metabolic rate by 10% and after 8 months had little other effect. 1 g. per kg. body-wt. increased the basal metabolic rate of rats by 84% and caused death in 3—4 days. (**II**) is present in the bile and colon of dogs after fatal, massive doses of (**I**). R. S. C.

Di-*p*-aminophenyl sulphone. A. M. VanArendonk and E. C. Kleiderer (*J. Amer. Chem. Soc.*, 1940, **62**, 3521—3522).—Thioaniline (purified by means of the disulphate) is converted by boiling Ac_2O–AcOH and then H_2O_2–AcOH at 40—50° into $(p\text{-}NHAc\cdot C_6H_4)_2SO_2$, m.p. 275—278°, which in boiling 10% HCl gives $(p\text{-}NH_2\cdot C_6H_4)_2SO_2$, m.p. 175—176°. R. S. C.

Synthesis of vitamin-*A*. M. V. Krauze and J. M. Slobodin (*J. Gen. Chem. Russ.*, 1940, **10**, 907—912).—Axerophthol prepared from β-ionylideneacetaldehyde (**I**) and CMe_2:CH·CHO (method: Kuhn *et al.*, A., 1937, II, 288) is biologically inactive. β-Ionone and $(OEt)_2CH\cdot CH_2\cdot MgBr$ in Et_2O (4 hr. at the b.p.) give (**I**) in 50—64% yield. R. T.

Formation of insoluble digitonides of cholesterol derivatives. F. S. Spring and G. Swain (*Nature*, 1940, **146**, 718).—A *cis*-3 : 4-dihydroxy-Δ^5-cholestene monobenzoate, m.p. 153—154°, which differs from that (m.p. 209—210°) described by Rosenheim *et al.* (A., 1937, II, 191), has been isolated. It fails to give a digitonide under conditions which effect immediate pptn. of the digitonides of cholesterol (**I**) and the *cis*-diol. Hence the formation of one of the monobenzoates has been accompanied by migration of Bz from the $C_{(3)}$- to the $C_{(4)}$-OH. The introduction of a C_4-*cis*-OBz group into (**I**) prohibits the digitonin reaction. L. S. T.

Derivatives of homoanisic acid. A. Burger and S. Avakian (*J. Org. Chem.*, 1940, **5**, 606—609).—Addition of *p*-$C_6H_4Me\cdot COCl$ to CH_2N_2 in Et_2O at room temp. gives p-*anisyl CHN*$_2$ *ketone*, m.p. 90—91°, transformed by conc. aq. NH_3 and 10% $AgNO_3$ in dioxan at 60—70° into *p*-OMe·C_6H_4·CH_2·CO·NH_2, m.p. 188—189°, which is hydrolysed (KOH–EtOH) to homoanisic (*p*-anisylacetic) acid (**I**), m.p. 86—87°, the overall yield being 53%. $ClSO_3H$ at −5° to 0° and then at 40° converts (**I**) into 3-*chlorosulphonylhomoanisic acid*, m.p. 164—165° (yield 80·6%), reduced by Zn dust and H_2SO_4 at −5° to 80° to 3-*thiol*-p-*homoanisic acid* (**II**), m.p. 83—84°. The structure of (**II**) is proved thus: 3 : 4 : 1-$NO_2\cdot C_6H_3$(OMe)·CH_2Cl is converted by KCN in EtOH containing a little KBr into 3-*nitro*-4-*methoxyphenylacetonitrile*, m.p. 87—87·5°, which is hydrolysed (50% H_2SO_4–AcOH) to 3-*nitro*-p-*homoanisic acid*, m.p. 132—133°, also prepared from (**I**) and conc. HNO_3 in glacial AcOH. This is reduced (H_2–Raney Ni–EtOH) to 3-*aminohomoanisic acid*, m.p. 110—111°, converted by diazotisation and boiling with 40% H_2SO_4 into homo*iso*vanillic acid, m.p. 127—128°, and by diazotisation and treatment with alkaline Na_2S_2 into 3 : 3′-dithiohomoanisic acid, which is reduced (Zn dust and glacial AcOH at 100°) to (**II**). 1 : 3 : 2-$C_6H_3MeBr\cdot NO_2$ is oxidised by $Na_2Cr_2O_7$ and boiling dil. H_2SO_4 to 2 : 3 : 1-$NO_2\cdot C_6H_3Br\cdot CO_2H$, m.p. 250—251°. This and (**II**) are dissolved in KOH–MeOH, the solution is evaporated to dryness, and the residue is heated at 190°, thereby yielding 2′-*nitro*-3′-*carboxy*-2-*methoxydiphenyl sulphide*-5-*acetic acid*, m.p. 232—234° (decomp.), which is reduced by $Fe(OH)_2$–aq. NH_3 to the 2′-NH_2-*acid*, m.p. 222—224°. H. W.

Lactones related in structure to cardiac aglucones: the lactone of β-aldehydo-β-*cyclo*pentylpropionic acid. S. K. Ranganathan (*Current Sci.*, 1940, **9**, 458—459).—The method of Fried *et al.* (A., 1940, II, 312) has been applied to the prep. of β-aldehydo-β-*cyclo*pentylpropionic acid (**I**) (cf. A., 1939, II, 321). OMe·CH_2·CN and Mg *cyclo*pentyl bromide yield *cyclopentyl OMe·CH*$_2$ *ketone*, b.p. 192—194°/680 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 130°), which with Zn and $CH_2Br\cdot CO_2Et$ gives *Et β-hydroxy-γ-methoxy-β-*cyclo*pentylbutyrate*, b.p. 140°/6 mm., and this with HBr in AcOH followed by distillation yields (?) β-cyclo*pentyl*-Δ^{β}-*buteno*-γ-*lactone*, b.p. 155°/5 mm., which with 3% KOH–MeOH furnishes (**I**). F. R. G.

Benzyl β-dimethylamino-α-phenyl-α-ethylpropionate (hydrochloride, m.p. 167—168°).—See A., 1941, III, 128.

Stereochemical studies. XXII. Decomposition of optically active α-phenylethylthiolacetic acids. B. Holmberg (*Arkiv Kemi, Min., Geol.*, 1940, **14**, A, No. 2, 12 pp.).—Various routes for the transitions: CHPhMe·S·CH_2·CO_2H (**I**) ⇄ CHPhMe·OH (**II**) have been studied with reference to optical stability and inversion. With $CH_2Br\cdot CO_2Na$ followed by hydrolysis, (−)-(**I**) gives (+)-(**II**) (60—80% racemised); with SH·CH_2·CO_2H this material gives inactive (**I**). (+)-(**I**) is racemised by $HgCl_2$ in N-HCl and the (**II**) formed is inactive, but the product from (−)-(**I**) and $HgSO_4$ has slight (+)-rotation. (+)-(**II**) with SO_2Cl_2 yields (−)-CHPhMeCl (**III**) (60% racemised) which is reconverted into (**I**) [still slightly (+)] by SNa·CH_2·CO_2Na. (+)-(**I**) with Br in glacial AcOH gives (−)-CHPhMeBr (**IV**), $[\alpha]_D^{20}$ −46° (calc.); this racemises very rapidly. (−)-(**III**) (NaOH) and (−)-(**IV**) (H_2O) give (+)-(**II**). The results are discussed. M. H. M. A.

Preparation of *o*-nitrobenzoic acid.—See B., 1941, II, 30.

Beckmann rearrangement of 2 : 4-dihydroxybenzhydroxamic acid derivatives. A. W. Scott and W. O. Kearse (*J. Org. Chem.*, 1940, **5**, 598—605).—2 : 4 : 1-$(OH)_2C_6H_3\cdot CO_2H$ is converted by MeOH and HCl at room temp. into the Me ester (**I**), m.p. 76° (lit. 126—128°), and by boiling $SOCl_2$ followed by ice into 2 : 4-*dihydroxybenzoyl chloride* (**II**), m.p. 142°. 2 : 4-*Dihydroxybenzhydroxamic acid* (**III**), m.p. 162°, decomp. 171° (very difficult to purify), is prepared by the successive addition of NH_2OH,HCl and (**I**) to aq. KOH at room temp. or, better, by addition of free NH_2OH to a suspension of (**II**) in light petroleum (low b.p.). Attempts to prepare the benzoate of (**III**) were unsuccessful but the *acetate*, m.p. 188° (slight decomp.), is obtained by addition of AcCl to a cooled solution of the Na salt of (**III**) in H_2O or by cautious fusion of (**III**) with Ac_2O. KOEt in abs. EtOH transforms this substance into the *K* salt, explodes at 84°, which rearranges in H_2O at 90° to 1 : 5-*dihydroxybenzoxazole* (*hydroxyoxy-*

carbonil) (**IV**), m.p. 288°. The following scheme is suggested : $(OH)_2C_6H_3\cdot C(OM):NO\cdot COR \rightarrow (OH)_2C_6H_3\cdot C(:N-)\cdot O- \rightarrow (OH)_2C_6H_3\cdot N:C\cdot O \rightarrow$ (**IV**), whereas *o*-hydroxybenzazide rearranges thus : $OH\cdot C_6H_4\cdot CON_3 \rightarrow OH\cdot C_6H_4\cdot C(:O)\cdot N< \rightarrow OH\cdot C_6H_4\cdot N\cdot C:O \rightarrow OH\cdot C_6H_4\cdot N:C:O$. H. W.

Preparation of thiolcarboxylic acids and their arylamides. I. V. Hopper, J. H. MacGregor, and F. J. Wilson (*J. Soc. Dyers and Col.*, 1941, **57**, 6—9).—The following arylamides are best prepared (unless stated otherwise) from the acid (1 mol.), NH_2Ar (2 mols.), and PCl_3 in C_5H_5N (cf. A., 1939, II, 505). *o*-$SH\cdot C_6H_4\cdot CO_2H$ (**I**) gives an *anilide*, m.p. 236—237°, o-, m.p. 217—218°, and p-*toluidide*, m.p. 230° (both prepared using P_2O_5–PhMe), o-*chloroanilide*, m.p. 218—219°, o-*anisidide*, m.p. 156—157°, 4-*methoxy*-2-*methylanilide*, m.p. 233—234°, and α-, m.p. 247—248°, and β-*naphthylamide*, m.p. 167—168°. *p*-$SH\cdot C_6H_4\cdot CO_2H$ (prep. from the intermediate S_2-acid by aq. NaOH–$Na_2S_2O_4$; cf. Thompson, A., 1925, i, 815) affords an *anilide*, m.p. 263—264°, 4-*methoxy*-2-*methylanilide*, m.p. 235—236°, and β-*naphthylamide*, m.p. 282—283°. 2 : 3-$SH\cdot C_{10}H_6\cdot CO_2H$ (**II**) [prep. as for (**I**); Allen *et al.*, Org. Syntheses, 1932, **12**, 76] gives an *anilide*, m.p. 285—286°, o-, m.p. 279—280°, and p-*toluidide*, m.p. 276—277°, o-*anisidide*, m.p. 220—221°, α-*naphthylamide*, m.p. 306—307°, and 4-*chloro*-2 : 5-*dimethoxy*-, m.p. 255—256°, 4-*methoxy*-2-*methyl*-, m.p. 264—265°, and 2-*methoxy*-5-*diethylaminosulphonyl*-*anilide*, m.p. 214—215°. 1 : 8-$C_{10}H_6\langle^{S}_{CO}$ (**III**) is obtained in good yield from diazonaphthostyril (suspension distinctly acid to Congo-red) and Na_2S_x at >5°; 1 : 8-$SH\cdot C_{10}H_6\cdot CO\cdot NHAr$ could not be prepared from (**III**). Cotton yarn, impregnated with arylamides of (**I**) or (**II**) in aq. EtOH–KOH, and treated with diazotised bases, gives dyeings of biscuit, lemon, or fawn [from (**I**)] or biscuit, orange, or tan [from (**II**)], which do not possess all-round fastness properties. A. T. P.

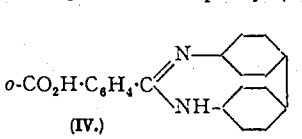
Anæsthetics of the naphthalene series. II. Esters of 4-alkylamino-1-naphthoic acids. S. I. Sergievskaja and K. P. Preobrashenskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 950—958).—1 : 4-$NH_2\cdot C_{10}H_6\cdot CO_2K$ and RI yield the acids 1 : 4-$NHR\cdot C_{10}H_6\cdot CO_2H$ [R = *Et*, m.p. 153° (decomp.), Pr^{α}, m.p. 172—173°, Bu^{α}, m.p. 208°, *allyl*, m.p. 151°], which are esterified in the usual way to 1 : 4-$NHR\cdot C_{10}H_6\cdot CO_2R'$ [R = Et, R' = *Et*, m.p. 76—77° (*hydrochloride*, m.p. 145—146°), Pr^{α}, m.p. 69° (*hydrochloride*, m.p. 143—145°), $NEt_2\cdot CH_2\cdot CH_2$, m.p. 188—189°; R = Pr^{α}, R' = *Et*, m.p. 38—39° (*hydrochloride*, m.p. 156°), $NEt_2\cdot CH_2\cdot CH_2$ (*hydrobromide*, m.p. 182—183°); R = Pr^{β}, R' = $NEt_2\cdot CH_2\cdot CH_2$ (*hydrobromide*, m.p. 185—186°); R = Bu^{α}, R' = *Et*, m.p. 54° (*hydrochloride*, m.p. 143—144°), Pr^{α}, m.p. 50·5° (*hydrochloride*, m.p. 114—116°), $NEt_2\cdot CH_2\cdot CH_2$ (*hydrobromide*, m.p. 180°); R = allyl, R' = *Et*, m.p. 67·5° (*hydrochloride*, m.p. 147—148°, decomp.), Pr^{α}, m.p. 61—62°, $NEt_2\cdot CH_2\cdot CH_2$ (*hydrobromide*, m.p. 191—191·5°)]. The activity of the $NEt_2\cdot CH_2\cdot CH_2$ esters is > of alkyl esters. R. T.

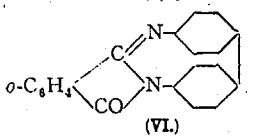
4-Hydroxy-3-sulphobenzoic acid. G. V. Medox and N. K. Dobrovolskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 705—706).—*p*-$OH\cdot C_6H_4\cdot CO_2H$ and 10% oleum (30 min. at 100°) afford 4 : 3 : 1-$OH\cdot C_6H_3(SO_3H)\cdot CO_2H$ in 98% yield. R. T.

Preparation of *m*-carboxybenzenesulphondichloroamide and of carboxybenzene-3 : 5-bis(sulphondichloroamide) from benzoic acid. O. V. Vasilevskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 683—684).—BzOH and $ClSO_3H$ yield *m*-$CO_2H\cdot C_6H_4\cdot SO_2Cl$, which with aq. NH_3 gives the sulphonamide, chlorinated to *m*-*carboxybenzenesulphondichloroamide*. BzOH and $ClSO_3H$ in oleum–P_2O_5 yield 1 : 3 : 5-$CO_2H\cdot C_6H_3(SO_2Cl)_2$, from which the 3 : 5-*disulphonamide*, m.p. 249—250°, and 3 : 5-*bis*(*sulphondichloroamide*) are prepared as above. R. T.

Elimination of the phthalyl residue in Gabriel's synthesis [of amines]. A. A. Beer and N. K. Kotschetkov (*J. Gen. Chem. Russ.*, 1940, **10**, 714—717).—The method of Ing *et al.* (A., 1926, 1132) is preferred. R. T.

Products of condensation of phthalic anhydride with benzidine. B. A. Porai-Koschitz and P. M. Mostriukov (*J. Gen. Chem. Russ.*, 1940, **10**, 629—635).—Benzidine (**I**) and *o*-$C_6H_4(CO)_2O$ (**II**) in EtOH yield a mixture of *NN'*-4 : 4'-diphenylenephthalamic acid (**III**) and the substance (**IV**). (**III**) is obtained almost pure when (**I**) is added to fused (**II**), whilst (**IV**) is the sole product when (**II**) is added to fused (**I**). 4 : 4'-Diphthalimidodiphenyl (**V**) added to fused (**I**) yields the


(IV.)


(VI.)

substance (**VI**), which regenerates (**V**) when added to fused (**II**). R. T.

Preparation of $\Delta^{9:11}$-cholenic acid. S. Bergström (*Arkiv Kemi, Min., Geol.*, 1940, **14, B**, No. 6, 2 pp.; cf. Barnett *et al.*, A., 1938, II, 497).—The semicarbazone, m.p. 227—230° (decomp.), of 12-keto-$\Delta^{9:11}$-cholenic acid with NaOEt at 200°/10 hr. gives $\Delta^{9:11}$-*cholenic acid*, m.p. 154—155° (Me ester, m.p. 85—86°). W. McC.

2 : 4-Dihydroxybenzaldehyde-2 : 4-dinitrophenylhydrazone. A. W. Scott and J. M. Burns (*J. Amer. Chem. Soc.*, 1940, **62**, 3522).—This *substance* has m.p. 286° (decomp.). R. S. C.

Sulphanilamide compounds. V. Arylidene derivatives of N^4-acetyl-N^1-*p*-aminophenylsulphanilamide and N^1-*p*-aminophenylsulphanilamide. H. G. Kolloff and J. H. Hunter (*J. Amer. Chem. Soc.*, 1940, **62**, 3355—3357; cf. A., 1940, II, 327).—*Sulphanil*-p-*aminoanilide* (**I**), m.p. 155°, or its N^4-*Ac* derivative, m.p. 230—231°, with 1 mol. of PhCHO at 140° gives *sulphanil*-p-*benzylideneaminoanilide* (**II**), m.p. 225°, and its N^4-*Ac* derivative, m.p. 206·5—207°, respectively. *Sulphanil*-p-*anisylidene*- (**III**), m.p. 204—205° (N^4-*Ac* derivative, m.p. 246·5—247·5°), -p-p'-*dimethylaminobenzylidene*-, m.p. 214—215° (N^4-*Ac* derivative, m.p. 242°), and -p-p'-*nitrobenzylidene*-, m.p. 223—224° (N^4-*Ac* derivative, m.p. 255·5—257·5°), -*aminoanilide* are similarly prepared. With 2 mols. of ArCHO, (**I**) gives N^4-p-*anisylidenesulphanil*-p-p'-*anisylidene*-, m.p. 183—184°, N^4-p-*dimethylaminobenzylidenesulphanil*-p-p'-*dimethylaminobenzylidene*-, m.p. 238·2°, and N^4-p-*nitrobenzylidenesulphanil*-p-p'-*nitrobenzylidene*-, m.p. 230°, -*aminoanilide*, but the $(CHPh:)_2$ compound could not be obtained. The structure of (**II**) and (**III**) is proved by hydrogenation (Raney Ni) in dioxan at 50—58°/3 atm. to the known *p*-$NH_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_6H_4\cdot NH\cdot CH_2Ar$ (*loc. cit.*). R. S. C.

Orientation in the acylation of phenol and in the rearrangement of phenolic esters. A. W. Ralston, M. R. McCorkle, and S. T. Bauer (*J. Org. Chem.*, 1940, **5**, 645—659).—In the action of octoyl chloride on PhOH in presence of $AlCl_3$, the use of equimol. proportions of PhOH and $AlCl_3$ and hence of the complex $OPh\cdot AlCl_2$ (**I**) favours the production of the *o*-OH-ketone whilst if more $AlCl_3$ is used [hence if R·COCl,$AlCl_3$ (**II**) is present] the *p*-isomeride is preferentially produced. If both complexes are previously formed the acyl group shows a decided preference for the *p*-position. If (**II**) reacts with (**I**) the ratio *p*/*o* is >1. The previous formation of the complexes excludes the possibility of the reaction (**II**) + PhOH → R·COCl + (**I**) + HCl → $OH\cdot C_6H_4\cdot COR,AlCl_3$. When this possibility is excluded the yield of *p*-isomeride is materially increased. In presence of (**I**) but not of (**II**) in $C_2H_2Cl_4$ the yield of the isomerides is independent of the temp. over the range 50—100° but *o*-orientation is abnormally favoured at 30°. Similar results are obtained at 50° and 100° when the PhOH is added to the previously-formed (**II**) but at 30° the *p*/*o* ratio differs decidedly from that at 50° and 100°. Ester formation is the predominant reaction at the lower temp. but decreases with increase in the amount of $AlCl_3$ or temp. The presence of the ester as such during the reaction cannot be assumed since it may be formed by hydrolysis of the $AlCl_3$–ester complex. Ester formation may occur : (**I**) + R·COCl ⇌ $R\cdot CO_2Ph,AlCl_3$ (**III**) and (**III**) → $OH\cdot C_6H_4\cdot COR,AlCl_3$. Ester-complex formation proceeds very rapidly as compared with ketone-complex formation and if hydrolysis is effected at any intermediate point the product consists of a mixture of *o*- and *p*-OH-ketones and ester. Repetition of the work of Cox (A., 1930, 344) using Ph octoate (**IV**) with excess of $AlCl_3$ in excess of Ph_2O gives 85% of *p*-phenoxyoctophenone (**V**), 3·9% of *p*- (**VI**) and a trace of *o*-hydroxyoctophenone. The high yield of (**V**) is due to an intermol. reaction since (**VI**) is almost unaffected by treatment with 2 mols. of $AlCl_3$ in excess of Ph_2O for 6 hr. at 70°. Fries rearrangement of (**IV**) by $AlCl_3$ in $C_2H_2Cl_4$ gives a *p*/*o* ratio >1. Increase of temp. from 70° to 100° decreases the amount of ester without altering the ratio of isomerides. Increase in the amount of $AlCl_3$ increases

the *p*/*o* ratio. The rearrangement can be represented, $C_7H_{15}\cdot CO_2Ph + 2AlCl_3 \rightarrow$ (I) + (II) + HCl→ $C_7H_{15}\cdot CO\cdot C_6H_4\cdot O\cdot AlCl_2$. With mol. proportions of ester and $AlCl_3$ initial conditions favour the formation of the *p*-isomeride because of the great excess of $AlCl_3$ present but the later stages of the change are under conditions favouring the *o*-isomeride. The chain length of the acid group is not a significant influence in the rearrangement of Ph esters. $PhNO_2$, "Skellysolve *B*," $C_2H_2Cl_4$, and CS_2 are placed in order of increasing *ortho*-directing influence. Under the experimental conditions rearrangement of *p*- and *o*-OH-ketones is not observed. H. W.

4-*cyclo*Hexylbenzophenone and its oxime. R. D. Kleene (*J. Amer. Chem. Soc.*, 1940, **62**, 3523).—Phenyl*cyclo*hexane, BzCl, and $AlCl_3$ in CS_2 at room temp. and later 100° (bath) give 4-cyclo*hexylbenzophenone*, m.p. 58—60°, b.p. 195—200°/3 mm. (*oxime*, m.p. 125—127°), oxidised by $Na_2Cr_2O_7$–H_2SO_4 to *p*-$C_6H_4Bz\cdot CO_2H$. R. S. C.

Quantitative study of the so-called "positive halogen" in ketones and esters. R. Altschul and P. D. Bartlett (*J. Org. Chem.*, 1940, **5**, 623—636).—Determinations have been made of the equilibrium const. and forward rate const. (under anti-oxidant conditions) for the debromination with HBr in glacial AcOH at 25° of CBz_3Br, $CPhBz_2Br$, CPh_2BzBr, CPh_3Br, $CHPh_2\cdot CBz_2Br$, $CMeBz_2Br$, $CHBz_2Br$, and $CBr(CO_2Et)_3$. This is regarded as typical of the so-called "positive halogen." The establishment of equilibrium in the bromination of $CHPh_2Bz$ is strongly promoted by light, indicating that there must be a peroxide-catalysed mechanism for the reverse reaction which, however, has not been detected. Peroxides are necessary to the reaction between HBr and CPh_3Br. However, compounds having Br in the α-position to :CO react with HBr at a rate which is independent of the concn. of peroxides or antioxidants (in presence of *cyclo*hexene) and is attributable to a polar mechanism, presumably the exact reversal of the bromination of a ketone through its enol in a polar solvent. Equilibrium and rate of debromination, which are greatly dependent on structure, do not show any general parallelism with one another. These results emphasise that there can be no sharp distinction between "positive" halogen and other halogen. In no case does the mode of reaction characteristic of "positive" halogen disappear but it may become very slow and the equilibrium may become unfavourable to its occurrence. H. W.

Mechanism of ketone formation from *trans*-indene glycol and halohydrins. C. M. Suter and H. B. Milne (*J. Amer. Chem. Soc.*, 1940, **62**, 3473—3477).—Measurement of the rate of formation of indan-2-one (I) from *cis*- and *trans*-indene glycol by acid indicates that the *trans*- is first isomerised to the *cis*-glycol which more slowly yields (I). Production of indan-1-one (II) from *trans*-indene bromohydrin in acid is more complex, Br′ being liberated faster than (II) is formed; simultaneous formation of glycol [and hence (I)] renders a quant. interpretation difficult. R. S. C.

Sterols. CXIII. Sapogenins. XLII. Conversion of sapogenins into pregnenolones. R. E. Marker (*J. Amer. Chem. Soc.*, 1940, **62**, 3350—3352).—Conversion of sapogenins into ψ-derivatives by Ac_2O at 200° is nearly quant. Subsequent oxidation by CrO_3–AcOH and hydrolysis (KOH–EtOH) to Δ^{16}-pregnen-3-ol-20-ones gives good (38—56%) yields if defined conditions are adhered to (cf. following abstract); protection of the ethylenic linking is unnecessary. *epi*-Sarsasapogenin acetate thus gives Δ^{16}-*pregnen*-3(α)-*ol*-20-*one* (I) (52%), m.p. 194—196° (*acetate*, m.p. 96—99°). Tigogenin, *epi*tigogenin, sarsasapogenin, and diosgenin acetates gives Δ^{16}-*allo*pregnen-3(β)-ol-20-one (II) (49%), m.p. 202—204°, Δ^{16}-*allo*pregnen-3(α)-ol-20-one (56%) (III), m.p. 219—222°, Δ^{16}-pregnen-3(β)-ol-20-one (IV) (48%), m.p. (anhyd.) 188—190°, and $\Delta^{5:16}$-pregnadien-3(β)-ol-20-one (38%), m.p. 212—214°, respectively. Similarly dihydro-ψ-*epi*sarsapogenin, -ψ-sarsasapogenin, -ψ-tigogenin, and -ψ-*epi*tigogenin by acetylation and oxidation yield (I) (61%), (IV) (47%), (II) (60%), and (III) (56%), respectively. Na–EtOH and (I) give pregnane-3(α) : 20(α)-diol, m.p. 242—243° (diacetate, m.p. 175—176°). H_2–Pd–$BaSO_4$ reduces (I) in EtOH–Et_2O to pregnan-3(α)-ol-20-one, m.p. 145—147° (acetate, m.p. 112—114°), whilst H_2–PtO_2 at 45 lb. in AcOH gives pregnane-3(α) : 20(β)-diol, m.p. 231°. Oxidation (CrO_3–AcOH) of (I) affords Δ^{16}-pregnene-3 : 20-dione, m.p. 200—202°. R. S. C.

Sterols. CXII. Sapogenins. XLI. Preparation of trillin. Its conversion into progesterone. R. E. Marker and J. Krueger (*J. Amer. Chem. Soc.*, 1940, **62**, 3349—3350).—Diosgenin, bromoacetylglucose, and $Hg(OAc)_2$ in boiling C_6H_6 give trillin tetra-acetate (I), m.p. 197°, identical with that (m.p. 199—200°) from the natural product (A., 1940, II, 378) and hydrolysed by 2% KOH–MeOH to trillin (~50% yield). *Sarsasapogenin* α-d-*glucoside tetra-acetate*, m.p. 227°, and the free *glucoside*, m.p. 245°, are similarly prepared. Ac_2O and (I) at 200° give a non-cryst. ψ-derivative, which with CrO_3–AcOH at 25° gives a product, converted by hydrolysis (conc. HCl–EtOH) and treatment with Girard's reagent into $\Delta^{5:16}$-pregnadien-3-ol-20-one, m.p. 210—212°; protection of the ethylenic linking is unnecessary. Hydrogenation (Pd–$BaSO_4$; Et_2O; 15 lb.) then gives Δ^5-pregnen-3-ol-20-one, m.p. 188—190°, which with Pt–black in CO_2 at 250—300° gives progesterone, m.p. 120—121°. R. S. C.

Steroids. IV. Degradation products of cholic acid and synthesis of 7 : 12-dihydroxyprogesterone. M. Ehrenstein and T. O. Stevens (*J. Org. Chem.*, 1940, **5**, 660—673).—Oxidation of diphenyl-3(α) : 7 : 12-triacetoxyternorcholylcarbinol with CrO_3 in AcOH gives an acidic portion hydrolysed by KOH–aq. MeOH to *ætiocholic* [3(α) : 7 : 12-*trihydroxyætiocholanic*] *acid* (I), m.p. 254—258°, $[\alpha]_D^{27.5}$ +65·2° in abs. EtOH, and a neutral portion from which Girard's reagent *T* removes 3(α) : 7 : 12-triacetoxypregnan-20-one (II), m.p. 149—151° (lit. 134—135°). Oxidation of (I) by CrO_3–AcOH affords *dehydroætiocholic* [3 : 7 : 12-*triketoætiocholanic*] *acid*, m.p. 245—246°. (II) is hydrolysed to 3(α) : 7 : 12-trihydroxypregnan-20-one, which is oxidised (CrO_3 in AcOH) to *pregnane*-3 : 7 : 12 : 20-*tetraone*, m.p. 238—242°, $[\alpha]_D^{26}$ +76·3° in $COMe_2$. Cautious alkaline hydrolysis of (II) yields 12-*acetoxypregnane*-3(α) : 7-*diol*-20-*one*, m.p. 230—233°, $[\alpha]_D^{27}$ +81·6° in $COMe_2$, oxidised to 12-*acetoxypregnane*-3 : 7 : 20-*trione*, m.p. 160·5—163·5°, $[\alpha]_D^{26}$ +125·9° in $COMe_2$, and converted by successive treatments with $Al(OPr^{\beta})_3$ in PhMe and *cyclo*hexanone and Ac_2O–C_5H_5N at 100° into 7 : 12-*diacetoxypregnane*-3 : 20-*dione* (III), m.p. 256—262°, $[\alpha]_D^{24}$ +113·7° in $CHCl_3$. Br and a little 40% HBr in AcOH transform (III) into somewhat impure 4-*Br*-derivative, m.p. 210—218° (decomp.), debrominated in collidine at ~190° to somewhat impure 7 : 12-*diacetoxy*-Δ^4-*pregnene*-3 : 20-*dione* (7 : 12-*diacetoxyprogesterone*), m.p. 249·5—252°. H. W.

2-Guanidinoanthraquinone.—See B., 1941, II, 36.

Reaction of naphthazarin with hexadiene and piperylene. B. Arbusov and K. Nikanorov (*J. Gen. Chem. Russ.*, 1940, **10**, 649—652).—Naphthazarin with $(CHMe{:}CH)_2$ (2 hr. at 160—170°) or $CH_2{:}CH\cdot CH{:}CHMe$ (20 hr. at 125—130°) in $PhNO_2$ yields 5 : 8-*dihydroxy*-1 : 4-*dimethyl*-, m.p. 226—227°, or 5 : 8-*dihydroxy*-1-*methyl*-*anthraquinone*, m.p. 236—237°, respectively. With *allo*cimene in EtOH the product is 1 : 4-*dihydroxy*-8-α-*methylpropenyl*-5 : 5-*dimethyl*-5 : 8 : 5a : 8a-*tetrahydroanthraquinone*, m.p. 157°. R. T.

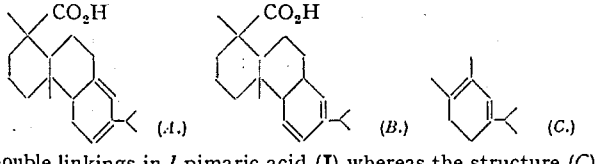
III.—TERPENES.

New degradation of cineolic acid. H. Rupe and R. Zweidler (*Helv. Chim. Acta*, 1940, **23**, 1025—1045).—The action of Mg aryl or alkyl halides on cineolic anhydride (I) consists exclusively of addition to CO attached to $C_{(6)}$. Addition of one or two radicals is a question of constitution. In the first case a CO-acid is produced which is immediately reduced to the OH-acid by the Grignard compound. In the second case a OH-acid is produced. Addition of (I) to MgPhBr (2 mols.) in Et_2O affords 6-*diphenylcarbinyleucalyptanic acid* (II), $OH\cdot CPh_2\cdot CMe<\begin{matrix}CH_2\cdot CH_2\\O—CMe_2\end{matrix}>CH\cdot CO_2H$, m.p. 162—163°, also formed with cineolic acid when 1 mol. of MgPhBr is used. (The name "eucalyptan" is proposed for the parent 2 : 2 : 6-trimethyltetrahydropyran.) (II) is transformed by KOH–Me_2SO_4 into the *Me* ester (III), m.p. 90—91°, and by boiling Ac_2O into the *lactone*, m.p. 133—134°, which is converted by HBr in MeOH into a very unstable *compound*, $C_{23}H_{27}O_2Br$, transformed by C_5H_5N into *Me benzhydryl*-Δ^5-*eucalyptenate*, preferably obtained from (III) and P_2O_5 in boiling C_6H_6. The corresponding *acid*, m.p. 145°, is oxidised by $KMnO_4$ to $CPh_2Me\cdot CO_2H$, m.p. 172° (p-*toluidide*, m.p. 110—111°), and a little terebinic acid (II) which alone is produced by the action of O_3. (III) is oxidised by CrO_3 to $COPh_2$ and (IV) (*Ag* salt; p-*toluidide*, m.p. 186—187°). *p*-$C_6H_4Me\cdot MgBr$ and (I) yield

6-*di*-p-*tolylcarbinyleucalyptanic acid*, m.p. 151—152°, whilst 6-*di*-p-*benzyl*-, m.p. 137—138°, and 6-*di*-1′-*naphthyl*-, m.p. 210—212°, *-carbinyleucalyptanic acid* are similarly derived. (I) and MgMeBr or MgMeI afford 6-*dimethylcarbinyleucalyptanic acid*, m.p. 110—111° (*Me* ester, b.p. 139—141°/12 mm.). The corresponding *lactone*, b.p. 146—148°/12 mm., m.p. 77—78°, is reduced by Na in boiling EtOH to 3-*hydroxymethyl*-6-*dimethylcarbinyleucalyptan*, a viscous liquid which could not be distilled without loss of H_2O. (II) and MgEtBr give 6-*diethylcarbinyleucalyptanic acid*, m.p. 137·5—138°, b.p. 188°/11 mm. (slight decomp.) (*Mg*, *Ca*, and *Cd* salts). The *lactone* (V), m.p. 89—90°, b.p. 163—165°/14 mm., is hydrolysed with difficulty by NaOH and is not reduced by H_2–Pd–C in $COMe_2$ or H_2–Ni–EtOAc at 90°/170 atm. Boiling HI (*d* 1·57) gives very unstable compounds containing I. The *Me* ester (VI), b.p. 162—165°/15 mm., is very stable towards boiling Ac_2O or HCO_2H. It is converted by $SOCl_2$ or PCl_5 into a very unstable *Cl*-ester, better obtained from (V) and MeOH–HCl. It is almost unaffected by attempted hydrogenation (Pd–$BaSO_4$; Zn–Cu; Zn–Pd in EtOH) and a Cl-free product is obtained only with difficulty by C_5H_5N. The corresponding unstable *Br*-ester is transformed by boiling C_5H_5N into *Me methyldiethyl*-Δ^5-*eucalyptenate*, b.p. 139—141°/10 mm. [better obtained from (VI) and P_2O_5], which could not be hydrogenated (Pd–$BaSO_4$ or Ni). Incautious treatment of (V) with HBr may cause fission of the pyran ring followed by replacement of the OH produced by Br, giving a compound transformed by C_5H_5N into a doubly unsaturated *compound*, $C_{15}H_{28}O_2$, b.p. 123—127°/10 mm. The non-cryst. *diethylmethyl*-Δ^5-*eucalyptenic acid* (VII) loses some CO_2 when distilled under diminished pressure and passes at atm. pressure into (?) 6-*methyldiethyl*-Δ^5-*eucalyptene*, b.p. 104—107°/14 mm. Ozonisation of (VII) in CCl_4 or, preferably, oxidation with $KMnO_4$ yields (IV). (VII) is with difficulty reduced (Na salt–Ni–H_2 at 142°/200 atm.) to 6-*methyldiethyleucalyptanic acid*, a liquid (*Me* ester, b.p. 147—150°/11 mm.), accompanied by a neutral *liquid*, $C_{13}H_{28}O$, b.p. 119—121°/11 mm. $MgPr^{\alpha}Br$ and (I) yield 6-*di*-, m.p. 111—112°, and 6-*mono*-, m.p. 179°, *-propylcarbinyleucalyptanic acid*, the latter arising from the reduction of a primary CO-acid by a second mol. of $MgPr^{\alpha}Br$. (I) and $MgPr^{\beta}Br$ afford a resin and 6-iso*propylcarbinyleucalyptanic acid*, m.p. 114—115° (*Ag* salt; *lactone*, m.p. 119—120°); it is hydrogenated (Ni–H_2 at 125°/185 atm.) to $\beta\delta$-*dimethyl*-η-iso*propyloctane*-$\gamma\delta\theta$-*triol*, m.p. 59—60°, which consumes 1·09 mol. of $Pb(OAc)_4$ and is oxidised by CrO_3 to 6-iso*butyryleucalyptan*-3-*carboxylic acid*, m.p. 86—87° (transformed by MgEtBr into 6-α-*hydroxy*-α-iso*propyl*-n-*propyleucalyptan*-3-*carboxylic acid*, m.p. 150—152°), and (IV). Mg *cyclo*hexyl bromide and (II) give 6-cyclo*hexylcarbinyleucalyptanic acid*, m.p. 180—181° (*Ag* salt; *Me* and p-*bromophenacyl*, m.p. 109—111°, esters). p-*Nitrobenzylthiuronium chloride*, m.p. 217—218°, yields *derivatives*, $C_{20}H_{31}O_6N_3S$, m.p. 151—152°, and $C_{22}H_{35}O_6N_3S$, m.p. 130—131°, with dimethyl- and diethylcarbinyleucalyptanic acid. H. W.

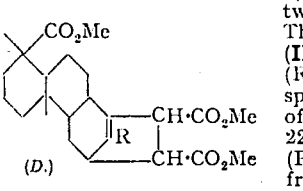
Degradation of *iso*borneol by the xanthate method. A. I. Schavrigin (*J. Gen. Chem. Russ.*, 1940, **10**, 807—811).—*iso*Bornyl or bornyl xanthate decomposes at 210—220°, giving bornylene in 40—50% yield. R. T.

Diterpenes. XLIII. Position of the double linkings of *l*-pimaric acid. L. Ruzicka and S. Kaufmann (*Helv. Chim. Acta*, 1940, **23**, 1346—1356; cf. A., 1940, II, 184).—Two possibilities (*A*) and (*B*) remain for the distribution of the



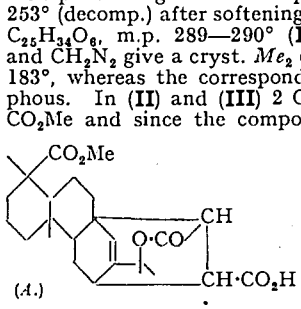
(*A.*) (*B.*) (*C.*)

double linkings in *l*-pimaric acid (I) whereas the structure (*C*) is no longer tenable. Preference is accorded to (*A*) particularly with respect to the transformation of (I) into abietic acid since (*B*) postulates the wandering of the two double linkings over two C atoms. Ozonisation of the Me_3 ester of the adduct (II) of (I) and maleic anhydride in AcOH at room temp. and decomp. of the ozonide with H_2O gives small amounts of amorphous acids and a mixture of neutral products from which a singly unsaturated *ketotricarboxylic ester* (III), $C_{26}H_{36}O_7$, m.p. 168—169 (*oxime*, m.p. 174—176°), and a doubly unsaturated tricarboxylic *ester* (IV), $C_{27}H_{38}O_6$, m.p. 124—126°, which gives a marked yellow colour with $C(NO_2)_4$ have been isolated. Hydrogenation (PtO_2 in AcOH) of (IV) causes absorption of 2 H with re-formation of (II). Since loss of CH_2 occurs during the production of (III) it is therefore probable that ozonisation follows an unusual course. The most probable hypothesis is the entry of OH into Pr^{β} followed by elimination of H_2O during ozonisation yielding $\cdot CMe{:}CH_2$ which can react with O_3 with production of Ac. The ultraviolet absorption spectrum of (III) proves it to be an $\alpha\beta$-unsaturated ketone and the double linking of (II) is therefore in conjugation to the CO of the degradation product. The location of CO in a side-chain is proved by treatment of (III) with NaOBr in alkaline solution, whereby 2 CO_2Me are hydrolysed with production of $CHBr_3$ and a *Me* H_3 *tetracarboxylate* (V), $C_{23}H_{30}O_8{\cdot}0{\cdot}5H_2O$, m.p. 280—283°, converted by CH_2N_2 into a Me_4 ester, $C_{26}H_{36}O_8$, m.p. 152—153°. The absorption spectrum of (V) shows the bands characteristic of $\alpha\beta$-unsaturated acids and that of (IV) exhibits those required for two conjugated double linkings. The structures of (I), (IV), and (III) are represented by (*D*) (R = Pr^{β}, $CMe{:}CH_2$, and Ac respectively). Partial hydrolysis of (III) gives a Me_2 *H* ester, m.p. 226—228°, and hydrogenation (PtO_2 in AcOH) affords a mixture from which the *hydroxytricarboxylic ester*, $C_{26}H_{36}O_7$, m.p. 128—129°, can be isolated; in this compound the double linking can be detected by $C(NO_2)_4$ since it is no longer vicinal to CO. Reduction (Clemmensen) of (III) and dehydrogenation (Se) of the non-cryst. product gives a hydrocarbon, m.p. 86—87°, which must be 1-*methyl*-7-*ethylphenanthrene* [additive *compound* with $C_6H_3(NO_2)_3$, m.p. 131—133°] provided that isomerisations have not occured during the transformations. Treatment of (III) with a large excess of MgEtI and dehydrogenation (Se) of the resulting product yields similarly 1-*methyl*-7-sec.-*butylphenanthrene*, m.p. 60—62° [additive *compound*, m.p. 121—123°, with $C_6H_3(NO_2)_3$], oxidised (CrO_3 in AcOH) to the *quinone*, $C_{19}H_{18}O_2$, m.p. 138—140°. All m.p. are corr. H. W.

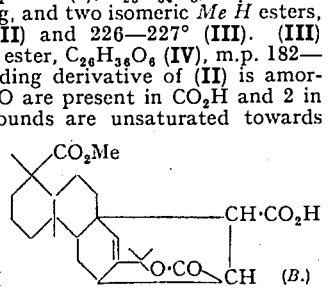


(*D.*)

Diterpenes. XLIV. Action of ozone and permanganate on the additive product of maleic anhydride and *l*-pimaric acid. L. Ruzicka and W. A. Lalande, jun. [with S. Kaufmann] (*Helv. Chim. Acta*, 1940, **23**, 1357—1366; cf. A., 1933, 279; 1938, II, 287; Wienhaus *et al.*, A., 1936, 1385).—Ozonisation in AcOH of the additive product of maleic anhydride and Me *l*-pimarate gives the compound (I), $C_{25}H_{34}O_8$, m.p. 252—253° (decomp.) after softening, and two isomeric *Me H* esters, $C_{25}H_{34}O_6$, m.p. 289—290° (II) and 226—227° (III). (III) and CH_2N_2 give a cryst. Me_2 ester, $C_{26}H_{36}O_6$ (IV), m.p. 182—183°, whereas the corresponding derivative of (II) is amorphous. In (II) and (III) 2 O are present in CO_2H and 2 in CO_2Me and since the compounds are unsaturated towards

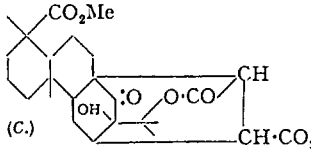


(*A.*)



(*B.*)

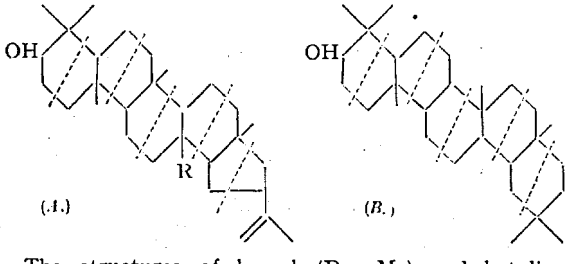
$C(NO_2)_4$ it is probable that the remaining 2 O are present in a difficultly hydrolysed lactone group. For (II) and (III) the formulæ (*A*) and (*B*) are probable whilst (I) is possibly (*C*). The presence of CO in (I) is now recognised spectroscopically but the group is hindered so that it does not react with the customary ketonic reagents. Oxidation of (I) by $KMnO_4$ (O = 1) fails to give the compound, $C_{24}H_{34}O_7$, m.p. 191—192°, recorded by Arbusov (A., 1933, 392), its place being taken by two *lactonedicarboxylic acids*, $C_{24}H_{32}O_8$ (V), m.p. 211—212°, and $C_{24}H_{34}O_8$ (VI), m.p. 250—252° after softening. (V) gives a yellow colour with $C(NO_2)_4$ and titrates as a dibasic acid, the lactone group being hydrolysed with difficulty; its Me_2 ester, m.p. 182—184°, is identical with (IV). The lactone group of (VI) is hydrolysed by N-KOH. With CH_2N_2 (VI



(*C.*)

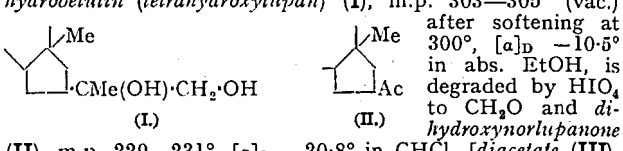
yields a Me_2 ester (**VII**), m.p. 218—220°. Neither (**VI**) nor (**VII**) gives a yellow colour with $C(NO_2)_4$. The constitution of (**VI**) remains obscure. The action of $KMnO_4$ (O = 2) on (**I**) gives (**V**) in 75% yield whereas with $KMnO_4$ (O = 3) a *substance*, $C_{24}H_{32}O_8$ (**VIII**), m.p. 307—308° (decomp.), results in 12—18% yield. (**VIII**) does not give a yellow colour with $C(NO_2)_4$, is titrated as a monobasic acid, and with CH_2N_2, gives a Me_1 ester, $C_{25}H_{34}O_8$, m.p. 276—278°. Acid and ester are readily hydrolysed, whereby 3 CO_2H are identified. In addition to CO_2H (**VIII**) therefore contains an anhydride group. Two further O atoms are probably present as OH since warm Ac_2O and C_5H_5N give a *diacetate*, $C_{28}H_{34}O_{10}$, m.p. 273—275°, although in very poor yield. 2 OH are also detected by Zerevitinov's method. The function of the final O is not explained. Reaction products could not be obtained with NH_2OH or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ but the presence of strongly masked CO is not excluded. All m.p. are corr. H. W.

Triterpenes. LIV. Lupenal and lupenalol and their further transformations. L. Ruzicka and G. Rosenkranz (*Helv. Chim. Acta*, 1940, **23**, 1311—1324; cf. A., 1940, II, 137).—Replacement of C_6H_6 by AcOH in the oxidation of lupeol acetate by SeO_2 (*loc. cit.*) leads to the more rapid production in better yield of *lupenalol acetate* (**I**) (formerly "ketolupeol acetate"), m.p. 224—226°, $[\alpha]_D$ +4·2° in $CHCl_3$, the aldehydic nature of which is established by its oximation, with simultaneous hydrolysis, to *lupenaloloxime*, m.p. 245—246°, $[\alpha]_D$ +2° in $CHCl_3$, which is converted by Ac_2O at 120° into *acetyl-lupenolonitrile*, m.p. 254°, $[\alpha]_D$ +18·6° in $CHCl_3$; the absorption spectrum of this compound is very closely similar to that of 17-cyano-3-acetoxy-$\Delta^{5:16}$-androstadiene which contains an $\alpha\beta$-unsaturated nitrile. Oxidation of α-lupene (**II**) (Heilbron *et al.*, A., 1938, II, 195) with SeO_2 in AcOH affords *lupenal* (**III**), m.p. 203°, $[\alpha]_D$ +4·3° in $CHCl_3$ [*hydrazone*, m.p. 214—216° (decomp.)], the absorption spectrum of which closely resembles that of lupenalol (**IV**). The formation of an $\alpha\beta$-unsaturated aldehyde from a compound with semicyclic CH_2 requires a migration of the double linking into the ring; this is rendered the more improbable in the present case by the re-formation of lupeol and (**II**) by the Wolff–Kishner treatment of (**IV**) and (**III**). Further the oxidative degradation of (**I**) confirms the absence of semicyclic CH_2 and renders probable the presence of ·CMe:CH_2; (**I**) and CrO_3 in AcOH give a saturated acetoxymonocarboxylic acid (**V**), $C_{30}H_{48}O_4$, m.p. 271—272°, $[\alpha]_D$ −17·6° in dioxan [Me ester (**VI**), m.p. 236—237°, $[\alpha]_D$ −17·1° in dioxan], which is not hydrogenated (PtO_2) and does not give a yellow colour with $C(NO_2)_4$. Alkaline hydrolysis of (**VI**) gives *Me bisnorlupanolate*, m.p. 221—223°, $[\alpha]_D$ −13·6° in dioxan, whilst similar treatment of (**V**) affords bisnorlupanolic acid (**VII**), $C_{28}H_{46}O_3$, m.p. 261—262°, $[\alpha]_D$ −14·1° in dioxan. Confirmation of the presence of ·CMe:CH_2 in lupeol is given by the formation of $COMe_2$ by oxidation with CrO_3, the ·CMe:CH_2 passing partly into :CMe_2 in presence of the acid reagent. Decision between the C_{28} and C_{30} formulæ (*loc. cit.*) for (**VII**) is effected only with difficulty by analysis but readily by titration. This has not been effected with (**VII**) but the analogous *bisnorlupanic acid*, m.p. 238—240° (vac.), $[\alpha]_D$ −8·8° in $CHCl_3$, is thus shown to be $C_{28}H_{46}O_2$. Hydrolysis of acetylnorlupanolone with KOH–MeOH yields norlupanolone, m.p. 234—236°, $[\alpha]_D$ −14·6° in $CHCl_3$ (*oxime*, m.p. 243—244°). All m.p. are corr.

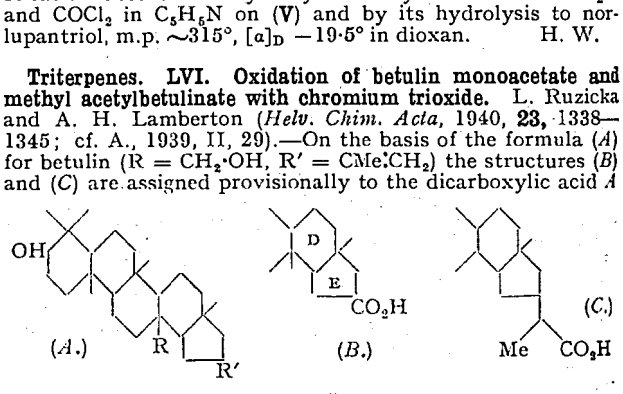


The structures of lupeol (R = Me) and betulin (R = ·CH_2·OH) are provisionally represented by (*A*), which passes by ring enlargement of the *cyclo*pentano-group into the structure (*B*) of the oleanolic group. H. W.

Triterpenes. LV. Products of the oxidation of betulin and betulin diacetate. L. Ruzicka and M. Brenner (*Helv. Chim. Acta*, 1940, **23**, 1325—1337).—The double linking of betulin can be hydroxylated (Crieger) and the so-formed *dihydroxydihydrobetulin* (*tetrahydroxylupan*) (**I**), m.p. 303—305° (vac.) after softening at 300°, $[\alpha]_D$ −10·5° in abs. EtOH, is degraded by HIO_4 to CH_2O and *dihydroxynorlupanone* (**II**), m.p. 229—231°, $[\alpha]_D$ −20·8° in $CHCl_3$ [*diacetate* (**III**), m.p. ~190°, $[\alpha]_D$ −11·0° in $CHCl_3$]. Oxidation of betulin diacetate (**IV**) with CrO_3 affords, as neutral product, (**III**), which does not give cryst. derivatives with NH_2OH or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ but in which the presence of :CO is established by the absorption spectrum and by reduction (H_2–PtO_2–AcOH at room temp.) to *diacetoxynorlupanol* (**V**), m.p. 252—254°, $[\alpha]_D$ −11·1° in $CHCl_3$, oxidised to the ketone. The acid products of the oxidation are separated as their Me esters, whereby *Me* (+)-*diacetoxylupanate*, m.p. 234—236°, $[\alpha]_D$ +18·9° in $CHCl_3$, and *Me* (−)-*diacetoxylupanate*, m.p. 213—214°, $[\alpha]_D$ −48° in $CHCl_3$, are obtained. Further, the acids can be separated from one another by stepwise extraction with alkali or by fractional dissolution of them adsorbed on Al_2O_3. *Me* (+)-*dihydroxylupanate* has m.p. 248—249°, $[\alpha]_D$ +4·9° in $CHCl_3$. With H_2O_2 and (**IV**) there result the two isomeric acids and a mixture of neutral compounds from which only *formyldiacetoxynorlupanol*, m.p. 235—237°, $[\alpha]_D$ −8·4° in $CHCl_3$, has been isolated. Its constitution is established by its synthesis by the action of HCO_2H and $COCl_2$ in C_5H_5N on (**V**) and by its hydrolysis to norlupantriol, m.p. ~315°, $[\alpha]_D$ −19·5° in dioxan. H. W.



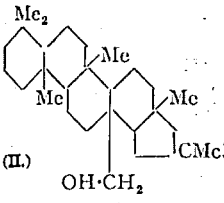
Triterpenes. LVI. Oxidation of betulin monoacetate and methyl acetylbetulinate with chromium trioxide. L. Ruzicka and A. H. Lamberton (*Helv. Chim. Acta*, 1940, **23**, 1338—1345; cf. A., 1939, II, 29).—On the basis of the formula (*A*) for betulin (R = CH_2·OH, R′ = CMe:CH_2) the structures (*B*) and (*C*) are assigned provisionally to the dicarboxylic acid *A*



(**I**) and acetyldicarboxylic acid *E* (**II**) obtained (*loc. cit.*) by the oxidation of betulin monoacetate (**III**) with CrO_3. The oxidation of (**III**) and acetylbetulic acid with CrO_3 is described. Treatment of Me acetylbetulate with CrO_3 in AcOH at 80—90° gives the Me_1 ester of (**II**), m.p. 259—260°, which does not give a colour with $C(NO_2)_4$ and is converted by CH_4N_2 into the Me_2 ester of (**II**), m.p. 243—245°, $[\alpha]_D$ +19° in $CHCl_3$; hydrolysis (KOH–MeOH) of the products insol. in alkali gives the Me_1 ester of (**I**), m.p. 274—276°, which does not give a colour with $C(NO_2)_4$ and is converted by CH_2N_2 into the Me_2 ester of (**I**), m.p. 178—180°, $[\alpha]_D$ −60°±6° in $CHCl_3$. The neutral oxidation product is identified as *Me norlupanolonate* (cf. *A*, R = CO_2Me; R′ = Ac), m.p. 250—252°, $[\alpha]_D$ −33° in $CHCl_3$, which is unchanged by boiling N-KOH–MeOH and does not give a yellow colour with $C(NO_2)_4$. It is converted by boiling Ac_2O into a substance, m.p. ~235° after softening at 205°; it does not give cryst. compounds with NH_2OH or $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$. (**I**) is transformed by Ac_2O–C_5H_5N into its acetate, m.p. ~310°, which is dehydrogenated (Se at 355—370°) to 1 : 5 : 6-$C_{10}H_5Me_3$. This, with a *substance*, (?) $C_{29}H_{46}O_2$, m.p. 240—241°, which does not give a colour with $FeCl_3$, is obtained similarly from (**II**). M.p. are corr. H. W.

Triterpenes. LVII. 2-Deoxybetulin and 2-deoxy*allo*betulin. L. Ruzicka and S. D. Heinemann (*Helv. Chim. Acta*, 1940, **23**, 1512—1518; cf. preceding abstract).—Betulin 2-monoacetate (**I**) is transformed by BzCl in C_5H_5N at 100° into *betulin 2-acetate x-benzoate*, m.p. 205·5—206°, which could not be smoothly hydrolysed to the Ac-free benzoate. (**I**) and PhNCO in boiling C_6H_6 give *betulin 2-acetate x-phenylcarbamate*, m.p. 226·5—227°, hydrolysed by 2% K_2CO_3 in boiling 75% MeOH to *betulin 2-phenylcarbamate*, m.p. 239·5—240·5°. This is oxidised by CrO_3 in AcOH to *betulone 2-phenylcarbamate*, m.p. 226·5—227° [*oxime*, m.p. 257·5—258°; *azine*,

$C_{60}H_{96}O_2N_2$, m.p. 356—357° (decomp.)], which is transformed by N_2H_4,H_2O, followed by C_5H_{11}·ONa in C_5H_{11}·OH at 200°, into *2-deoxybetulin* (**II**), m.p. 140—141°, $[\alpha]_D$ +16°±2° in $CHCl_3$ (*acetate*, m.p. 164—164·5°; *formate*, m.p. 133—135°). This is cyclised by 100% HCO_2H in $CHCl_3$ at 100° to *2-deoxyallobetulin*, m.p. 234—235°, $[\alpha]_D$ +54° ± 1° in $CHCl_3$, also obtained by the successive action of N_2H_4,H_2O and Na in C_5H_{11}·OH at 200—210° on *allo*betulone (**III**); in EtOH (**III**) is transformed into the *azine*, $C_{60}H_{96}O_2N_2$, m.p. 364—365°. All m.p. are corr.



(II.)

H. W.

Triterpenediols. IV. Constitution of onocerin. J. Zimmermann (*Helv. Chim. Acta*, 1940, **23**, 1110—1113).—The previous hypothesis (A., 1938, II, 372) that the conversion of α- into β-onocerin (**I**) consists of a transformation of a tetra- into a penta-cyclic structure cannot be maintained since titration of (**I**) with BzO_2H discloses the presence of two double linkings. Ozonisation of α-onocerin diacetate and treatment of the ozonide with steam gives CH_2O and a substance not volatile in steam which is hydrolysed (KOH–EtOH) to a *compound*, $C_{28}H_{45}O_4$, m.p. 217° (*diacetate*, m.p. 165°, and its *dioxime*, m.p. 265°). Similar treatment of β-onocerin diacetate gives $COMe_2$ and a non-cryst. resin which affords a minute amount of yellow crystals when hydrolysed (KOH–EtOH).

H. W.

Triterpene resinols and related acids. XII. Oxidation of β-amyradienyl-I acetate with selenium dioxide, a new route to Jacobs' keto-diol, $C_{30}H_{44-46}O_3$. C. W. Picard and F. S. Spring (*J.C.S.*, 1941, 35—39).—The prep. of β-amyradienol-I from β-amyrenonol (reduction with Na–EtOH or C_5H_{11}·OH) is accompanied by the formation of β-amyradienol-II, identical with the compound obtained by oxidation (SeO_2) of β-amyradienyl esters. The two ethylenic linkings as a conjugated system are located in -I in a single ring but in -II the system is not contained in a single ring. Oxidation (SeO_2) of β-amyradienyl-I acetate gives the keto-acetate, $C_{32}H_{46(48)}O_4$, of Jacobs and Fleck (A., 1930, 1292). Oxidation (Br–AcOH) of β-amyrenonyl benzoate affords *β-amyradienonyl benzoate*, m.p. 251—252°, hydrolysed (KOH) to *β-amyradienonol* (**I**), m.p. 239—240°; the *acetate*, m.p. 255°, is oxidised ($KMnO_4$) to an *acetate*, $C_{32}H_{48}O_4$, m.p. 234—235° (slight decomp.), not identical with Jacobs' keto-acetate. A provisional structure is assigned to (**I**).

F. R. S.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Mytiloxanthin, m.p. 140—144° (block; corr.).—See A., 1941, III, 123.

Nature of Haslewood's hepatols. H. B. MacPhillamy (*J. Amer. Chem. Soc.*, 1940, **62**, 3518—3519).—Hog liver yields β-7-hydroxycholesterol and Haslewood's hepatol (**I**), m.p. 277—279° (A., 1939, III, 707). However, (**I**) is digitogenin (*diacetate*, m.p. 231—233°), derived from digitonin by Haslewood's method of isolation. The second hepatol (*loc. cit.*) is probably impure (**I**).

R. S. C.

Hydrogenation of lignin. E. E. Harris (*Paper Trade J.*, 1940, **111**, *TAPPI Sect.*, 297—298).—The % of MeOH, *n*-propyl*cyclo*hexane derivatives (**I**), high-boiling resin, and H_2O obtained by hydrogenating various lignins in dioxan + Cu chromite are tabulated. With isolated sulphite and sulphate lignin S acts as a catalyst poison but it is possible to remove S as H_2S or MeSH and to hydrogenate the resulting products. H_2O containing Ni may also be used as solvent. The products are similar to those obtained in dioxan but OMe is less extensively removed. At higher temp. OH and OMe are eliminated with production of *n*-propyl*cyclo*hexane. Wood chips are completely converted into oils and products sol. in H_2O when hydrogenated at about 250°/5000 lb. MeOH, PrOH, and reduced carbohydrates are found in the portion sol. in H_2O; the identified oils consist of (**I**). At lower temp. and pressure hydrogenation can be controlled so that only a small proportion of gas is absorbed; a pulp remains.

H. W.

Sclerotiorin, $C_{20}H_{20}O_5Cl$ (?), metabolic product of *Penicillium sclerotiorum*, von Beyma.—See A., 1941, III, 138.

V.—HETEROCYCLIC.

Derivatives of furfuryl and tetrahydrofurfuryl alcohols. R. D. Kleene and S. Fried (*J. Amer. Chem. Soc.*, 1940, **62**, 3516).—*Furfuryl*, m.p. 75—77°, and *tetrahydrofurfuryl* p-*nitrobenzoate*, m.p. 46—48°, and *tetrahydrofurfuryl* 3 : 5-*dinitrobenzoate*, m.p. 83—84°, are prepared.

R. S. C.

Complex rotatory dispersion of optically active tetrahydrofuryl-2-carbinol.—See A., 1941, I, 74.

Coumarones and chromans.—See B., 1941, II, 37.

Structural interpretations of flavone spectra.—See A., 1941, I, 72.

Additive compounds of zinc, cadmium, cobalt, and nickel halides with 1 : 4-dioxan. R. Juhasz and L. F. Yntema (*J. Amer. Chem. Soc.*, 1940, **62**, 3522).—Anhyd. dioxan (**I**) gives additive *compounds*, (*a*) *X*,(**I**) in which X = $ZnCl_2$, $CdCl_2$, $CdBr_2$, CdI_2, $CoCl_2$, $NiCl_2$, and $NiBr_2$, (*b*) *X*,2(**I**), in which X = $ZnCl_2$, $ZnBr_2$, ZnI_2, $CoBr_2$, CoI_2, and NiI_2, and (*c*) $CdCl_2$,0·5(**I**), CoI_2,3(**I**), CoI_2,(**I**),+2 and $4H_2O$.

R. S. C.

Thianthren series. I. 2-Sulphothianthren sulphone and 2-chlorothianthren sulphone. V. V. Kozlov, E. P. Fruktova, and O. M. Schemjakina (*J. Gen. Chem. Russ.*, 1940, **10**, 1077—1088).—Thianthren sulphone and 62% oleum (5·5 hr. at 140—145°) yield *2-sulphothianthren sulphone* (**I**) [*Na*, $+H_2O$, *K*, +0·5, 1, and $3H_2O$; Cu^{II}, *Ba*, *Zn*, *Al*, Fe^{II}, Fe^{III}, Pb^{II}, *Ag* salts; *chloride*, m.p. 194° (decomp.); *amide*, m.p. 178°], which with PCl_5–$POCl_3$ (5 hr. at 180°) affords *2-chlorothianthren sulphone*, m.p. 120°. Fusion of (**I**) with NaOH (20 min. at 300°) yields PhOH, resorcinol, and *p*-OH·C_6H_4·SO_3H.

R. T.

Attempts to prepare 7-substituted *dicyclo*[1 : 2 : 2]-azaheptanes. G. R. Clemo and E. Hoggarth (*J.C.S.*, 1941, 41—47).—Et pyridine-4-carboxylate (*picrate*, m.p. 142°) and MgMeI give dimethyl-4-pyridylcarbinol (**I**) (*picrate*, m.p. 95°, *picrolonate*, decomp. 236°, and *platinichloride*, m.p. 194°), which could not be satisfactorily reduced with Na–EtOH, yielding a small amount of 4-*iso*propylpyridine (*picrate*, m.p. 135°, *picrolonate*, m.p. 208°, and *platinichloride*, m.p. 202°), not identical with 4-α-*methylvinylpyridine*, b.p. 82°/15 mm. [*picrate* (+EtOH), and *picrolonate*, m.p. 231°], prepared by dehydration (P_2O_5) of (**I**). Reduction of 4-acetylpyridine with $Pr^{\beta}OH$ and $Al(OPr^{\beta})_3$ affords *methyl*-4-*pyridylcarbinol*, m.p. 54° (*picrate*, m.p. 125°, *picrolonate*, m.p. 232°, and *platinichloride*, m.p. 206°), which could not be hydrogenated. *Et* 1-*acetylpiperidine*-4-*carboxylate*, b.p. 135—136°/1 mm., with MgMeI gives *dimethyl*-1-*acetyl*-4-*piperidylcarbinol*, b.p. 162—165°/1 mm., which could not be deacetylated. *Et* 1-*benzoylpiperidine*-4-*carboxylate*, m.p. 77°, and MgMeI yield in small amount a mixture of $COMe_2$ and *dimethyl*-4-*piperidylcarbinol* (**II**), m.p. 136° [*picrate*, two forms, m.p. 156° and 187°; *picrolonate*, m.p. 265° (decomp.)] HBr and (**II**) give 4-α-*bromoisopropylpiperidine*, m.p. 192°, which with Ag_2O or K_2CO_3 affords (**II**) and an *amine*, $C_8H_{15}N$, b.p. 58—62°/12 mm. (*picrolonate*, m.p. 221°), reduced (PtO_2–H_2) to 4-*iso*propylpiperidine. Et piperidine-4-carboxylate and MgMeI yield *4-acetylpiperidine* (?), b.p. 108—110°/25 mm. [*picrate*, m.p. 266° (decomp.), *picrolonate*, m.p. 206°, and *platinichloride* (+EtOH), m.p. 206°], not identical with that described by Prelog (A., 1938, II, 456); the base with MeI gives a *compound*, $C_7H_{13}ON,MeI$, m.p. 170°, which with Ag_2O yields a base, b.p. 108—109°/25 mm. (*picrolonate*, m.p. 215°).

F. R. S.

Cuprammine salts. D. A. Maruchian (*J. Gen. Chem. Russ.*, 1940, **10**, 917—920).—CuCl or CuBr and excess of C_5H_5N afford the *salts* $[Cu_2(C_5H_5N)_4]Cl_2$ (**I**) or $[Cu_2(C_5H_5N)_4]Br_2$ (**II**). With Cl_2 (**I**) gives $[Cu(C_5H_5N)_4]Cl_2$, also obtained from (**II**), via (**I**).

R. T.

Action of acid chlorides on tetrahydrofuran, and certain derivatives of δ-diethylaminobutan-α-ol. L. M. Smorgonski and J. L. Goldfarb (*J. Gen. Chem. Russ.*, 1940, **10**, 1113—1119).—Tetrahydrofuran and *p*-NO_2·C_6H_4·COCl or *p*-NO_2·C_6H_4·COBr (4 hr. at the b.p.) yield *δ-chlorobutyl*, b.p. 205—206°/7 mm., or δ-*bromobutyl* p-*nitrobenzoate*, b.p. 191—194°/3 mm., m.p. 45—46°. *δ-Bromobutyl acetate*, b.p. 95—96°/14 mm., obtained analogously, reacts with $NHEt_2$ yielding *δ-diethylaminobutyl acetate*, b.p. 112°/22·5 mm., hydrolysed to OH·$[CH_2]_4$·NEt_2 [*picrolonate*, m.p. 65—66°; p-*nitrobenzoate* (**I**) (*hydrochloride*, m.p. 158—159°; *picrate*, m.p. 151—152°)]. (**I**) is reduced ($SnCl_2$) to *δ-diethylaminobutyl* p-*aminobenzoate*,

an oil (*hydrochloride*, m.p. 171°). At room temp. (**I**) is rapidly converted into 1 : 1-diethylpyrrolidinium *p*-nitrobenzoate. R. T.

α-Nitropyridines. M. G. Bistritzkaja and A. V. Kirsanov (*J. Gen. Chem. Russ.*, 1940, **10**, 1101—1107).—When 5-chloro- or 5-bromo-2-aminopyridine is added to H_2O_2–H_2SO_4 at 0—5°, and the mixture is diluted after 48 hr. at room temp. and made neutral with aq. NH_3, 5-*chloro-*, m.p. 120·5—121°, or 5-*bromo*-2-*nitropyridine*, m.p. 149·5—150°, separates. These compounds yield the corresponding 2-aminopyridines when reduced with $Na_2S_2O_4$ or $SnCl_2$, whilst with As_2O_3 in aq. NaOH they give 5 : 5′-*dichloro-*, decomp. 204°, or 5 : 5′-*dibromo*-2 : 2′-*azoxypyridine*, decomp. 200°; with As_2O_3 and Na_3AsO_3 the products are 5 : 5′-*dichloro-*, decomp. 248°, and 5 : 5′-*dibromo*-2 : 2′-*azobenzene*, decomp. 235°. 3-Nitro-2-aminopyridine and aq. CH_2O at room temp. afford NN′-(3 : 3′-*dinitro*-2 : 2′-*dipyridyl*)*diaminomethane*. 5-Nitro-2-aminopyridine and aq. NaOCl yield a substance, $C_5H_5O_2N_3Cl_2$, probably a perchloride or a chloroamine, decomp. 60—80°. R. T.

Preparation of phenyl 2-pyridyl and 8-quinolyl sulphides and sulphones. H. C. Winter and F. E. Reinhart (*J. Amer. Chem. Soc.*, 1940, **62**, 3508—3511).—8-Chloro-5-nitroquinoline with Na_2S_2 in boiling EtOH gives *di-5-nitro-8-quinolyl disulphide*, m.p. 245°, and with PhSH or *p*-NO_2·C_6H_4·SH (**I**) and NaOAc in boiling EtOH gives *Ph*, m.p. 100°, and *p*-NO_2·C_6H_4 *5-nitro-8-quinolyl sulphide*, m.p. 223°, respectively. 2-Chloro-5-nitropyridine with PhSH at 135—150° gives Ph*, m.p. 121°, and with (**I**) and NaOAc in boiling EtOH gives p-NO_2·C_6H_4 *5-nitro-2-pyridyl sulphide*, m.p. 126—129°. Reduction of the appropriate NO_2-compound by $SnCl_2$–HCl yields Ph 5-amino-2-pyridyl*, m.p. 125—127° (lit. 120°), and 5-*amino*-8-*quinolyl**, m.p. 128° (*Ac* derivative, m.p. 97—98°), *sulphide*. H_2O_2 in AcOH oxidises the appropriate sulphide to *Ph* 5-*nitroquinolyl sulphoxide*, m.p. 145—146°, *Ph* 5-*nitro-**, m.p. 151—153° (m-NO_2-derivative, m.p. 169—170°), and 5-*amino*-2-*pyridyl sulphone**, m.p. 169—170°, p-NO_2·C_6H_4 5-*nitro*-2-*pyridyl sulphone*, m.p. 217°, *Ph* 5-*nitro-**, m.p. 180—181°, and 5-*amino*-8-*quinolyl sulphone**, m.p. 224° (*Ac* derivative, m.p. 268—269°). p-NO_2·C_6H_4 5-*nitro*-8-*quinolyl sulphone*, m.p. 237°, is prepared using CrO_3 (not H_2O_2) in AcOH first at room temp., later at b.p. 8-*Quinolinesulphonylsulphanilic acid**, +H_2O (Na salt), is also prepared. Compounds marked*, K 5-nitro-2-pyridinesulphonate, 5-amino-2-pyridinesulphonic acid, quinoline-8-sulphonic acid and its amide, 8-aminoquinoline-5-sulphonic acid, di-5-nitro-2-pyridyl and -8-quinolyl sulphide [prep. from 8-chloro-5-nitroquinoline by $CS(NH_2)_2$ and NaOEt] have no antistreptococcal activity. R. S. C.

6-Ethoxy-2 : 4-dimethylquinoline.—See B., 1941, II, 37.

Condensation of halogeno-pyridines, -quinolines, and -*iso*quinolines with sulphanilamide. M. A. Phillips (*J.C.S.*, 1941, 9—15).—When halogeno-pyridines, -quinolines, and -*iso*quinolines are condensed with *p*-NH_2·C_6H_4·SO_2·NH_2 (**I**) in presence of K_2CO_3–Cu, condensation generally occurs at the SO_2·NH_2 end of the mol., probably owing to the intermediate formation of the K salt of (**I**). In the absence of K_2CO_3, condensation occurs exclusively at the NH_2 end of (**I**). 2-Chloro-5-nitropyridine with (**I**) and K_2CO_3–Cu gives a mixture of 5-*nitro*-2-(p-*aminobenzenesulphonamido*)*pyridine*, m.p. 218—220° (*Ac* derivative, m.p. 279°), and p-(5′-*nitro*-2′-*pyridylamino*)*benzenesulphonamide*, m.p. 209—210° (*Na* salt; 5′-NH_2-derivative, m.p. 221°), the former predominating. The following are described: *Na* salt of 2-(*p*-aminobenzenesulphonamido)pyridine; 2-(p-*aminobenzenesulphonamido*)-*quinoline*, m.p. 194° (*Ac* derivative, m.p. 216°); p-(1′-*isoquinolylamino*)*benzenesulphonamide*, m.p. 275°; 1-(p-*aminobenzenesulphonamido*)*isoquinoline*, m.p. 263° (*Ac* derivative, m.p. 225°); 5-*amino*-2-(p-*aminobenzenesulphonamido*)*pyridine*, sinters 140—150°; and p-(2′-*pyridylamino*)*benzenesulphon*-2′-*pyridylamide*, m.p. 204°. F. R. S.

Heterocyclic amidines.—See B., 1941, II, 37, 37, 38.

Carbazole and its derivatives. I. Carbazolemonosulphonic acid. K. G. Mizutsch. **II. Bromination of carbazole and carbazole-3-sulphonic acid.** K. G. Mizutsch and A. J. Savtschenko (*J. Gen. Chem. Russ.*, 1940, **10**, 844—851, 852—854).—I. Carbazole (**I**) and KCNS in 96% AcOH are maintained for 1 hr. at 6—10°, and Br in AcOH is added gradually at 20° for 2 hr., yielding 3-thiocyanocarbazole (**II**), m.p. 111·7—112·7° (N-*Ac* derivative, m.p. 121—122°), also prepared by the Sandmeyer reaction from 3-*diazocarbazole thiocyanate*, m.p. 122—123° (decomp.). A by-product of the former reaction is 3 : 6(?)-*dithiocyanocarbazole*, m.p. 197·5—198·5° (N-*Ac* derivative, m.p. 196·5—197·5°). (**II**) is reduced (Zn in HCl–AcOH) to 3-*thiolcarbazole*, m.p. 199·5—202°. This is oxidised by **I** in AcOH to *dicarbazyl* 3 : 3′-*disulphide*, m.p. 240—241·5°, and by H_2O_2 in AcOH to *carbazole*-3-*sulphonic acid* (**III**) [*Na*, p-*chloroaniline*, m.p. 215·5—216·5°, *phenylhydrazine*, m.p. 223·2—223·8° (decomp.), α-$C_{10}H_7$·NH_2, m.p. 231—232°, β-$C_{10}H_7$·NH_2, m.p. 231—232°, *benzidine* salts].

II. Oxidation of (**I**) is not observed during bromination with $KBrO_3$–KBr; the products are mono-, di-, and 1 : 3 : 6-tri-bromocarbazole. (**III**) is brominated similarly to 1 : 3 : 8-*tribromocarbazole*-3-*sulphonic acid*, which with 3% HCl at 200° gives 1 : 3 : 8-*tribromocarbazole*, m.p. 178—180°. R. T.

Formation of pyrazolines from unsymmetrically substituted dibenzylideneacetones. L. C. Raiford and R. H. Manley (*J. Org. Chem.*, 1940, **5**, 590—597).—Condensation of αβ-diunsaturated unsymmetrical ketones containing the *p*-C_6H_4Cl·CH: and vanillylidene or substituted vanillylidene radicals with NHPh·NH_2 does not yield the phenylhydrazones but the isomeric pyrazolines. Oxidation ($KMnO_4$) of these gives invariably *p*-C_6H_4Cl·CO_2H and the required pyrazole-3-carboxylic acid, showing that the direction of rearrangement is away from the *p*-C_6H_4Cl·CH: radical. Vanillylideneacetone or its substitution product is mixed with *p*-C_6H_4Cl·CHO in EtOH and the liquid is kept for several hr. at 0° after being made strongly alkaline with NaOH; the Na salt which separates is treated with AcOH. Thus are obtained: *vanillylidene*-4′-*chlorobenzylideneacetone*, m.p. 137—138°, and its 5′-*Br-*, m.p. 191—192°, 6′-*Br-*, m.p. 179—180°, and 5′-NO_2-, m.p. 186—187°, derivatives. These are condensed with NHPh·NH_2 in glacial AcOH at room temp. for several days, thus giving the following *-pyrazolines*: 3-*phenyl*-1 : 5-*di*-p-*chlorophenyl-*, m.p. 135—136°; 5-*phenyl*-1 : 3-*di*-p-*chlorophenyl-*, m.p. 135—135·5°; 3-p-*chlorostyryl*-1-*phenyl*-5-4′-*hydroxy*-3′-*methoxyphenyl-*, m.p. 174°; 3-p-*chlorostyryl*-1-*phenyl*-5-5′-*bromo*-4′-*hydroxy*-3′-*methoxyphenyl-*, m.p. 170—171°; 3-p-*chlorostyryl*-1-*phenyl*-5-6′-*bromo*-4′-*hydroxy*-3′-*methoxyphenyl-*, m.p. 161—162°, and 3-p-*chlorostyryl*-1-*phenyl*-5-5′-*nitro*-4′-*hydroxy*-3′-*methoxyphenyl-*, m.p. 208—209°. Oxidation ($KMnO_4$ in C_5H_5N at room temp.) of the appropriate pyrazoline yields the following 1 : 5-*diphenylpyrazole*-3-*carboxylic acids* (substituents in C_6H_5 at $C_{(5)}$): 4′-*hydroxy*-3′-*methoxy-*, m.p. 165° after softening; 5′-*bromo*-4′-*hydroxy*-3′-*methoxy-*, m.p. 161—163°; 6′-*bromo*-4′-*hydroxy*-3′-*methoxy-*, m.p. 175°; 5′-*nitro*-4′-*hydroxy*-3′-*methoxy-*, m.p. ~90°. H. W.

Associating effect of the hydrogen atom. VII. N–H–N bond. Derivatives of pyrazole and indazole. H. T. Hayes and L. Hunter (*J.C.S.*, 1941, 1—5).—Contrasts in b.p., solubility in donor solvents, and degree of association are shown between derivatives of pyrazole and indazole possessing a free imino-H and those in which this atom has been replaced by an alkyl, aryl, or acyl group. The high vals. of these properties of the former class of compound are attributed to H-bond formation involving the imino-H. Cryoscopic measurement of mol. wt. of 16 derivatives is made over a range of concn. in C_6H_6 or $C_{10}H_8$ solution. A possible mechanism of pyrazole tautomerism is proposed. F. R. S.

2-Amino-1′ : 9′-pyrimidinoanthrone.—See B., 1941, II, 36.

Syntheses of carbaza-condensed systems from 2- and 6-aminonicotines. III. Reaction of bromopyruvic ester with 2- and 6-aminonicotine. J. L. Goldfarb and M. S. Kondakova. **IV. Condensation of 2-aminonicotine with acetoacetic ester.** M. S. Kondakova and J. L. Goldfarb (*J. Gen. Chem. Russ.*, 1940, **10**, 1055—1064, 1065—1068).—III. 2-Aminonicotine (**I**) in Et_2O and CH_2Br·CO·CO_2Et (12 hr. at room temp.) yield an additive product which when treated with boiling EtOH and then with K_2CO_3 gives 7-(1′-*methyl*-2′-*pyrrolidyl*)-2-*carbethoxy*-1-*azaindolizine*, b.p. 233—234°/6 mm., m.p. 96—97° (*hydrobromide*, m.p. 213—214°; *picrate*, m.p. 177—178°). This is hydrolysed (50% HCl; 20 hr. at the b.p.) to 7-(1′-*methyl*-2′-*pyrrolidyl*)-2-*carboxy*-1-*azaindolizine* [*mono-*, m.p. 198—201°, *di-hydrochloride*, m.p. 232—237°; *picrate*, m.p. 113—116°; *amide*, m.p. 225° (*dihydrochloride*, m.p. 244—254°)], readily losing CO_2 at 225—235°, to yield 7-(1′-*methyl*-2′-*pyrrolidyl*)-1-*azaindolizine*, b.p. 159°/5 mm., m.p. 44—47° [*dihydrochloride*, m.p. 257° (decomp.); *platinochloride*; *picrate*, m.p. 240°]. Nitration of this compound

gives 3-*nitro*-7-(1′-*methyl*-2′-*pyrrolidyl*)-2-*azaindolizine*, m.p. 96—97°, also obtained by hydrolysis of *Et* 3-*nitro*-7-(1′-*methyl*-2′-*pyrrolidyl*)-1-*azaindolizine*-1-*carboxylate* (II), m.p. 111—112°. (II) yields (I) when oxidised (CrO_3 in H_2SO_4) or when heated with KOH in EtOH. 6-Aminonicotine and $CH_2Br{\cdot}CO{\cdot}CO_2Et$ react as above, yielding *Et* 5-(1′-*methyl*-2′-*pyrrolidyl*)-1-*azaindolizine*-2-*carboxylate*, b.p. 235—237°/4 mm., m.p. 154° [*picrate*, m.p. 225° (decomp.)], which with 50% HCl (24 hr. at the b.p.) gives 5-(1′-*methyl*-2′-*pyrrolidyl*)-1-*azaindolizine*, b.p. 160°/4 mm. (*dipicrate*, m.p. 204—205°; *platinichloride*).

IV. (I) and $CH_2Ac{\cdot}CO_2Et$ (3·5 hr. at 170—185°) yield 2(4)-*keto*-9-(1′-*methyl*-2′-*pyrrolidyl*)-4(2)-*methyl*-1-*azaquinolizine*, m.p. 112° [*dipicrate*, m.p. 209°; *dihydrochloride*, m.p. 244—247° (decomp.); *platinichloride*], regenerating (I) when hydrolysed with 20% HCl or KOH–EtOH, and giving the 3-NO_2-derivative, m.p. 120—121°, with HNO_3–H_2SO_4. MeI adds on to the pyrrolidine-N, giving a *methiodide*, m.p. 238—240° (decomp.). R. T.

4-Glyoxalinyl-4′-hydantoylmethane and its hydrolysis. M. N. Schtschukina (*J. Gen. Chem. Russ.*, 1940, **10**, 1108—1112).—A solution of histidine (I) and $CO(NH_2)_2$ in H_2O is boiled for 5 hr., made acid with HCl, and evaporated to dryness. This gives 4(5)-*glyoxalinyl*-4′-*hydantoinylmethane*, m.p. 255° (*picrate*, m.p. 209°), which regenerates (I) when subjected to acid or alkaline hydrolysis. R. T.

Phthalocyanines.—See B., 1941, II, 40.

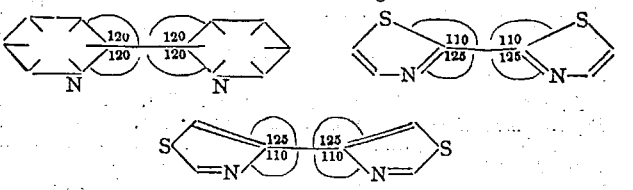
Preparation of aromatic oxazolidines. M. Meltsner, E. Waldman, and C. B. Kremer (*J. Amer. Chem. Soc.*, 1940, **62**, 3494—3495).—Boiling $OH{\cdot}[CH_2]_2{\cdot}NH_2$ (1) and ArCHO (1 mol.) in BuOH or BuOH–Bu_2O gives 2-*phenyl*-, b.p. 157°/24 mm., 2-*m*-, b.p. 159°/14 mm., and 2-*p*-*tolyl*-, b.p. 153°/15 mm., 2-*o*-, b.p. 195°/27 mm., and 2-*p*-*anisyl*-, b.p. 180°/12 mm., 2-*p*-*hydroxyphenyl*-, m.p. 169°, 2-*m*-, m.p. 73°, and 2-*o*-*nitrophenyl*-, m.p. 58°, *-oxazolidine*. *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ and *o*-$C_6H_4Cl{\cdot}CHO$ give additive *compounds*, b.p. 180°/13 mm., and 178°/22 mm., respectively. R. S. C.

2 : 6-Dimethylmorpholinoethyl alcohol.—See B., 1941, II, 38.

Polymethine dyes of the 3-hydroxythionaphthen series. II. Condensation of anils of 3-hydroxythionaphthen-2-aldehyde and its vinylene homologues with quaternary salts of 1-methylbenzthiazole. I. I. Levkoev, N. N. Sveschnikov, and V. V. Durmaschkina (*J. Gen. Chem. Russ.*, 1940, **10**, 773—778; cf. A., 1940, II, 381).—Polymethine dyes were prepared by the reaction *o*-C_6H_4<S—C(OH)>$C{\cdot}[CH{:}CH]_n{\cdot}CH{:}NPh$ + *o*-C_6H_4<S—NRI>$CMe \rightarrow HI + NH_2Ph$ + *o*-C_6H_4<S—CO>$C{:}CH{\cdot}[CH{:}CH]_n{\cdot}CH{:}C$<S—NR>$C_6H_4$-*o* [$n = 0$, R = *Me*, m.p. 249—250° (decomp.), R = *Et*, m.p. 212—214° (decomp.), R = Pr^{α}, m.p. 208—209° (decomp.), R = Bu^{α}, m.p. 177—178°; R = *Et*, $n = 1$, m.p. 219—220° (decomp.), $n = 2$, m.p. 177—178°]. The position of the band of max. absorption is not affected by varying R, but is shifted towards longer wave-lengths by increase in *n*. 1-Methylthiolbenzthiazole and *p*-$C_6H_4Me{\cdot}SO_3Et$ are heated (6 hr. at 130—140°), and the product is heated with 2-hydroxy-1 : 2-dihydrothionaphthen in EtOH, in presence of NaOAc (30 min. at the b.p.), yielding the *substance* *o*-C_6H_4<S—CO>$C{:}C$<S—NEt>C_6H_4-*o*, m.p. 214—216°. R. T.

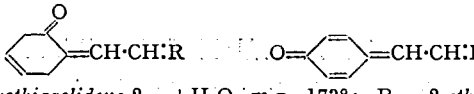
Benzoylmethyldibenzthiazyl 1-sulphide.—See B., 1941, II, 38.

Structure-chemical investigations. II. Structure of thiazole compounds and the Fe″-specific group. H. Erlenmeyer and H. Ueberwasser (*Helv. Chim. Acta*, 1940, **23**, 1268—1275).—Addition of solid $FeSO_4$ to a solution of 4 : 4′-dithiazolyl (I) in HBr in a closed vessel followed by NaOH gives the *compound*, $[Fe(C_6H_4N_2S_2)_2]Br_2{,}2H_2O$, pale red crystals which become yellow at 120°. Under these conditions 2 : 2-dithiazolyl (II) gives a *substance*, $[Fe(C_6H_4N_2S_2)_2]Br_2{,}2H_2O$, intensely coral-red crystals which are immediately decolorised by neutral H_2O. In these salts Fe has the co-ordination no. 4. The difference in the behaviour of dithiazolyls and dipyridyl (III) is attributed to the difference in the aromatic structure of C_5H_5N and thiazole. As a first approximation and taking account of the valency angle the following structures are assigned :



In (I) and (II) the valency angle of –N<C—C>N– differs appreciably from that in (III). Quinthiazole (IV) and $FeSO_4$ immediately give a lemon-yellow colour (capable of detecting 1 mg. Fe per l.) and the *bromide*, $[Fe(C_{10}H_6N_2S)_2]Br_2{,}2H_2O$, can be obtained in which Fe″ has the co-ordination no. 4. The group –N<C—C>N– in (IV) has not the Fe″-sp. structure which occurs in (III) and *o*-phenanthroline. H. W.

(A) Hydroxystyryl derivatives of quaternary heterocyclic salts. (B) Influence of the solvent on the colour of organic dye solutions. (C) Absorption spectra of cyanine dyes in the ultra-violet. A. I. Kiprianov and V. E. Petrunkin (*J. Gen. Chem. Russ.*, 1940, **10**, 600—612, 613—619, 620—628).—(A) *o*- or *p*-$OH{\cdot}C_6H_4{\cdot}CHO$ was condensed with the ethiodides of quinaldine, 1-methylbenzthiazole, and 4-phenyl-2-methyl- or 2 : 4-dimethyl-thiazole, in presence of C_5H_5N, to yield the following hydroxystyryl compounds: 2-*p*-, m.p. 257—258° (decomp.), or 2-*o*-*hydroxystyryl*-4-*methyl*-3-*ethyl*-, m.p. 215°, and 2-*p*-*hydroxystyryl*-4-*phenyl*-3-*ethyl*-*thiazole iodide*, m.p. 222—223° (decomp.), 1-*o*-, m.p. 241° (decomp.), or 1-*p*-*hydroxystyryl*-2-*ethylbenzthiazole iodide* (I), m.p. 246° (decomp.), and 2-*o*-, m.p. 198—200°, or 2-*p*-*hydroxystyryl*-1-*ethylquinoline iodide*, m.p. 232—233°. These iodides are converted by aq. KOH into the quinonoid dyes (*A*) [R = 4-*methyl*-3-*ethyl*-2 : 3-



dihydrothiazolidene-2-, $+H_2O$, m.p. 173°; R = 2-*ethyl*-1 : 2-*dihydrobenzthiazolidene*-2-, m.p. 140—145° (decomp.); R = 1-*ethyl*-1 : 2-*dihydroquinolidene*-2-, m.p. 160—163° (decomp.)], and (*B*) [R = 4-*methyl*-3-*ethyl*-2 : 3-*dihydrothiazolidene*-2-, $+H_2O$, m.p. 178° (decomp.); R = 4-*phenyl*-3-*ethyl*-2 : 3-*dihydrothiazolidene*-2-, m.p. 150—155° (decomp.)]. Bands of max. absorption are recorded for solutions of the quinonoid dyes in H_2O, EtOH, $CHCl_3$, and C_5H_5N; the colour of the solutions varies greatly according to the nature of the solvent used.

(B) Where resonance of apolar structure with bipolar ionic structure is possible, the colour of the solution depends on the μ of the solvent, which determines the composition of the equilibrium mixture.

(C) The absorption spectra of carbocyanine dyes of the types *o*-C_6H_4<Z—NMe>$C{\cdot}CH{:}CH{\cdot}CH{:}C$<Z—NMe>$C_6H_4$-*o* (Z = CH:CH, S, O, NMe, CMe_2), CH_2<S—$CH_2{\cdot}NMe$>$C{\cdot}CH{:}CH{\cdot}CH{:}C$<S—$CH_2$ / $NMe{\cdot}CH_2$>, or CH<S—$CMe{\cdot}NMe$>$C{\cdot}CH{:}CH{\cdot}CH{:}C$<S—$CH$ / $NMe{\cdot}CMe$> all exhibit bands in the ultra-violet (285—385 mμ.). The absorption spectra of the methiodides of *o*-C_6H_4<Z—N>CH or thiazole resemble those of the derived carbocyanine dyes. Max. absorption in the ultra-violet shifts towards longer wave-lengths with increase in length of the polymethine chain of the dyes *o*-C_6H_4<S—NMe>$C{\cdot}[CH{:}CH]_n{\cdot}CH{:}C$<S—NMe>$C_6H_4$-*o* ($n = 0$, 1, 2, 3). R. T.

Cyanine dyes.—See B., 1941, II, 40, 67.

[Stability of nicotinamide, nicotinuric acid, and trigonelline.]—See A., 1941, III, 118.

Resolution of racemic scopolamine into optical isomerides. M. N. Schtschukina, S. S. Okun, D. N. Jurigin, and N. A. Preobrashenski (*J. Gen. Chem. Russ.*, 1940, **10**, 803—806).—*dl*-Scopolamine di-*d*-camphorate, crystallised from H_2O, gives the l-*scopolamine* salt, m.p. 157—158°, $[\alpha]_D$ +18° in H_2O, from which *l*-scopolamine (**I**) is prepared. The residual *d*-salt in the mother-liquor is racemised, and (**I**) is separated from the racemate, as above. R. T.

Alkaloids of the Papaveraceæ family. VII. Alkaloids of *Papaver armeniacum*. Structure of armepavine. S. Junusov, R. A. Konovalova, and A. P. Orékhov (*J. Gen. Chem. Russ.*, 1940, **10**, 641—648).—Armepavine (**I**) and CH_2N_2 in MeOH yield *methylarmepavine*, m.p. 63—64°, $[\alpha]_D$ −84·48° in $CHCl_3$ [*methiodide* (**II**), m.p. 135—136°], oxidised by HNO_3 to anisic acid. (**II**) and KOH in MeOH (1 hr. at the b.p.) yield *de*-ON-*dimethylarmepavine*, m.p. 86° [*hydrochloride*, m.p. 229—230°; *methiodide* (**III**), m.p. 233—234°]. (**III**) when heated with KOH in MeOH gives NMe_3 and α-p-*anisyl*-β-(3 : 4-*dimethoxy*-6-*vinylphenyl*)*ethylene*, m.p. 79°, oxidised by $KMnO_4$ in $COMe_2$ to anisic acid and *m*-hemipinic acid. (**I**) and Et_2SO_4 yield *ethylarmepavine*, an oil, from which *p*-OEt·C_6H_4·CO_2H is obtained by oxidation with $KMnO_4$. (**I**) is oxidised similarly to *p*-OH·C_6H_4·CO_2H and 1-keto-6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline. (**I**) is therefore 6 : 7-dimethoxy-1-*p*-hydroxybenzyl-2-methyl-1 : 2 : 3 : 4-tetrahydro-*iso*quinoline. R. T.

Cinchona alkaloids in pneumonia. VIII. Sulphur derivatives of *apo*cupreicine ethers and aminoquinolines. (Miss) A. G. Renfrew and C. L. Butler (*J. Amer. Chem. Soc.*, 1940, **62**, 3304—3305).—The prep. and toxicity of p-*acetamido*-, m.p. 105°, and -*amino-benzenesulphonylhydroxyethyl*a*pocupreicine*, m.p. 99°, N-p-*acetamido*- and -*amino-benzenesulphonylquinicine*, 6-, m.p. 240°, and 8-*amino*-5-p-*sulphonamidophenylazoquinoline*, m.p. 245°, *ethyl*a*pocupreicine monohydrochloride*, cryst., $[\alpha]_D$ −26·7° in H_2O, hydroxyethyla*pocupreicine* dihydrochloride, cryst., and *quinicine monohydrochloride* are described. They have no useful antipneumococcic activity. Hydroxyethyla*pocupreicine*, a gum, $[\alpha]_D$ −29° in N-H_2SO_4, gives a *monohydrochloride*, +EtOH, m.p. 90°. R. S. C.

VI—ORGANO-METALLIC COMPOUNDS.

Organic mercury derivatives.—See B., 1941, III, 57.

VII.—PROTEINS.

Constitution of silk fibroin. K. H. Meyer, M. Fuld, and O. Klemm (*Helv. Chim. Acta*, 1940, **23**, 1441—1444).—Silk fibroin appears to contain only 10·8% of tyrosine instead of 13·2% recorded by Bergmann and Niemann (A., 1938, III, 210). *X*-Ray interferences of silk show that the crystallites have very appreciable length and comprise at least six identical periods in the direction of the fibre axis. The position within and without the chain can be represented by the scheme (G = glycyl, A = alanyl, T = tyrosyl, Ar = arginyl, S = seryl) G Ar G T G A G A G S G A G A G A G T Ar G.
amorphous in the crystallite amorphous
H. W.

Complex pseudoglobulin–lecithin in the vitellus.—See A., 1941, III, 204.

VIII.—ANALYSIS.

Quantitative capillary luminescence analysis.—See A., 1941, I, 90.

Systematic qualitative organic micro-analysis. Determinations of specific gravity. H. K. Alber (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 764—767).—The construction and use of micro-pipettes (capacities 100—6 cu.mm.) for determination of *d* are described. The accuracies obtained are sufficiently great for the identification of unknown liquids or solids. J. D. R.

Iodometric determination of small quantities of nitrogen without distillation.—See A., 1941, III, 64.

Apparatus for Van Slyke determination of amino-nitrogen in solid substances. O. Klemm and K. H. Meyer (*Helv. Chim. Acta*, 1940, **23**, 1444—1445).—The apparatus has been modified to allow the use of solid substances such as silk or wool. H. W.

Determination of micro-quantities of organic phosphorus. B. L. Horecker, T. S. Ma, and E. Haas (*J. Biol. Chem.*, 1940, **136**, 775—776).—1 μg. of P in protein is determined to ±3% by a modification of the method of Fiske *et al.* (A., 1926, 443), using the photo-electric spectrophotometer of Hogness *et al.* (A., 1937, I, 331). A. Lt.

Micro-tests for elements in organic compounds. II. Phosphorus, arsenic, and antimony. C. L. Wilson (*Analyst*, 1940, **65**, 405—406; cf. A., 1938, II, 301).—Org. mixtures containing P, As, and Sb are oxidised in a fusion mixture (1 Na_2O_2 : 2 KNO_3). P is identified as the double Mg NH_4 salt. As and Sb are distinguished by reduction with a Sn–Pt "couple" followed by a modified Gutzeit test. The elements are detected correctly in mixtures containing 5—20 μg. of P compound, 10—20 μg. of As compound, and 20—30 μg. of Sb compound. E. C. B. S.

Determination of boron in volatile organic compounds using the Parr oxygen bomb. W. M. Burke (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 50—51).—The sample mixed with Na_2CO_3 is oxidised in the Parr bomb and the H_3BO_3 determined by titration in presence of mannitol. The method provides a means of decomp. org. B compounds without the use of large amounts of reagent and gives accuracy ≮ previous methods. J. D. R.

Elimination of formaldehyde in the analysis of formaldehyde–formic acid mixtures. A. Hickling and F. Rodwell (*J.C.S.*, 1941, 51—52).—Most of the CH_2O is pptd. by excess of H_2S in strongly acid solution, H_2S removed by $CuSO_4$, and the excess of this pptd. by boiling with NaOH. The remaining CH_2O is determined by I titration and the CH_2O + HCO_2H with $KMnO_4$. A. Lt.

Analytical procedures employing Karl Fischer reagent. V. Determination of water in presence of carbonyl compounds. W. M. D. Bryant, J. Mitchell, jun., and O. M. Smith (*J. Amer. Chem. Soc.*, 1940, **62**, 3504—3505; cf. A., 1939, I, 577).—Aldehyde and ketone interference in the Karl Fischer titration for H_2O is inhibited by the presence of an excess of 2% HCN solution in C_5H_5N, the resulting cyanohydrins being inert towards the reagent. Analytical data for a series of 8 aldehydes and 5 ketones are given. W. R. A.

Microscopic identification of certain sugars and polyhydric alcohols. J. A. Quesne and W. M. Dehn (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 556—560).—Photomicrographs are reproduced of crystals of gentiobiose, *d*-lyxose, trehalose, dulcitol, mannitol, sorbitol, and binary mixtures of various sugars pptd. from saturated aq. solution by $COMe_2$, EtOH, MeCN, and dioxan. J. D. R.

Determination of pentoses. R. E. Reeves and J. Munro (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 551—553).—The pentose is boiled with HCl and xylene and the furfuraldehyde (**I**) in the xylene layer is determined colorimetrically with NH_2Ph,AcOH by comparison with standard solutions of (**I**) in xylene. 100% conversion of *d*-xylose into (**I**) is achieved. J. D. R.

Determination of methionine in certain mixtures. Precision method. J. J. Kolb and G. Toennies (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 723—724).—The purity of methionine can be determined with an accuracy of ±0·1% by oxidation with H_2O_2 in $HClO_4$ followed by determination of the unused H_2O_2 by KI–$Na_2S_2O_3$. The method is applicable to mixtures, as other NH_2-acids (except tryptophan, cysteine, and cystine) do not interfere. Procedure is detailed and data on the stability of H_2O_2 in 1—4N-$HClO_4$ are presented. J. D. R.

Photocolorimetric determination of furfuraldehyde. R. A. Stillings and B. L. Browning (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 499—502).—To a solution of neutral furfuraldehyde (**I**) in 20% NaCl is added NH_2Ph,AcOH and the transmittance of the red solution measured photometrically and compared with a known calibration curve. Beer's law is valid for concns. of (**I**) of 0·5—4·5 p.p.m. Methyl- and hydroxymethyl-furfuraldehyde introduce an error <1%, and CH_2O at 100 p.p.m. does not interfere. Procedure is detailed. J. D. R.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

APRIL, 1941.

I.—ALIPHATIC.

Electrochemical methods in organic chemistry. J. C. Beltz (*J. Chem. Educ.*, 1940, **17**, 516—518).—Conditions for the electrochemical prep. of numerous org. substances are tabulated. L. S. T.

Velocity of reaction of methane with steam.—See A., 1941, I, 118.

Action of elementary fluorine on organic compounds. IX. Vapour-phase fluorination of methane. E. H. Hadley and L. A. Bigelow (*J. Amer. Chem. Soc.*, 1940, **62**, 3302—3303; cf. A., 1940, II, 265).—CH_4 and F_2 in presence of Cu gauze give MeF, CH_2F_2, CHF_3, C_2F_6, and C_3F_8. The amount of liquid products is a max. (45%) from 2 : 1 : 10 F_2–CH_4–N_2. Const.-boiling mixtures, CHF_3–C_2F_6, b.p. −89°, CH_2F_2–C_3F_8, b.p. −58°, and MeF–C_2F_6, b.p. −89°, are recorded. Chain reactions, involving free radicals, are postulated. R. S. C.

Preparation and properties of trifluoromethyl compounds. J. H. Simons, R. L. Bond, and R. E. McArthur (*J. Amer. Chem. Soc.*, 1940, **62**, 3477—3480).—Passage of F_2 into CCl_4 (250 c.c.) and As (25 g.) at ~70° gives 74% of CF_4 and 17% of $CClF_3$; use of As (11 g.) and Br (3—4 c.c.) gives only CCl_3F; in both cases some C_6Cl_6 is formed. Passage of CCl_4 and F_2 over a Hg catalyst in a Cu tube at 340—370° (not As at 100° or AgF at 200—400°) gives $CClF_3$ in high yield. $CClF_3$ does not react with Mg in Et_2O or Li in C_6H_6 and other methods also failed to give $CF_3{\cdot}CO_2H$. Passage of $CClF_3$ over heated CaI_2 gives C, CaF_2, $CaCl_2$, and I. $CClF_3$ and KCN at 400—500° give only CF_4. IF_5 and CHI_3 at <0° rising to 80—90° give much CHF_3 and a little $CHIF_2$. Passage of CF_4 through an arc gives C_2F_6, C_3F_8, and other products (cf. Ruff *et al.*, A., 1933, 373). At 282°/3 mm. $(CF_3{\cdot}CO_2)_2Ba$ gives the same products as does the Na salt (Swarts, A., 1923, i, 292). $CBrF_3$ and ClF_3 are too unstable to be isolated. R. S. C.

Preparation and properties of ethylene. G. H. Stempel, jun. (*J. Chem. Educ.*, 1940, **17**, 508).—A method for the prep. of small vols. of C_2H_4 from Zn, $C_2H_4Br_2$, and EtOH is described. L. S. T.

Configuration of the Δ^{β}-butenes. M. H. Thomas and F. E. W. Wetmore (*J. Amer. Chem. Soc.*, 1941, **63**, 136—137).—Relative rates of reaction with $Hg(OAc)_2$ in H_2O or MeOH (deficiency of the reagent) at 0·8° confirm the view that the high- and low-boiling forms of $(CHMe{:})_2$ are the *cis*- and *trans*-forms, respectively. The latter form reacts the faster. cis-, m.p. 23·6°, and trans-*β-Chloromercuri-γ-methoxybutane*, m.p. 65·5°, and cis-, m.p. 59°, and trans-*β-chloromercuri-γ-hydroxybutane*, m.p. 80°, are prepared. R. S. C.

Preparation of higher *cis*- and *trans*-olefines. K. N. Campbell and L. T. Eby (*J. Amer. Chem. Soc.*, 1941, **63**, 216—219).—Hydrogenation of C_2R_2 in presence of Raney Ni in 95% EtOH at 60 lb. gives 70—90% of *cis*-$(CHR{:})_2$ (97—98% pure). Reduction by Na in liquid NH_3 gives 80—90% of *trans*-$(CHR{:})_2$ (100% pure). C_2Bu_2 is not reduced by granulated Zn in AcOH or HCl, or by Na–$C_5H_{11}{\cdot}OH$; Zn–Hg–HCl–AcOH gives a mixture containing Cl and an ester, doubtless formed by addition. Purity and configurations are determined by Raman spectra, f.p., and dielectric const. The *trans*-form has the lower *d* and f.p., but the two forms have similar b.p. and *n*. The following are recorded. Δ^{ϵ}-Decinene, f.p. −77°, b.p. 177·1—177·2°/751 mm.; Δ^{δ}-, f.p. −102°, b.p. 131·8—132·1°/747 mm., and Δ^{γ}-octinene, f.p. −104°, b.p. 132·8—133·0°/747 mm.; Δ^{γ}-hexinene, f.p. −101°, b.p. 81·2—81·3°/747 mm. cis-, f.p. −112°, b.p. 169·5—169·6°/739 mm., and trans-Δ^{ϵ}-*Decene*, b.p. −73°, b.p. 170·2°/739 mm. *cis*-, f.p. −118°, b.p. 121·7°/739 mm., and *trans*-Δ^{δ}-Octene, f.p. −84°, b.p. 121·4°/739 mm. cis-, f.p. −126°, b.p. 122·3°/741 mm., and trans-Δ^{γ}-*Octene*, f.p. −107°, b.p. 122·4°/741 mm. *cis*-, f.p. −135°, b.p. 66·8—66·9°/741 mm., and *trans*-Δ^{γ}-Hexene, f.p. −113°, b.p. 67·4—67·6°/741 mm. R. S. C.

Laboratory synthesis of ethyl chloride. I. A. Koten (*J. Chem. Educ.*, 1940, **17**, 461).—The prep. of EtCl by heating EtOH, $CaCl_2$, and Et_2SO_4 is described. L. S. T.

Chlorofluoropropanes. E. T. McBee, A. L. Henne, H. B. Hass, and N. Elmore (*J. Amer. Chem. Soc.*, 1940, **62**, 3340—3341).—CMe_2F_2 and Cl_2 at <0° in light or 60—70° in the dark give successively $CMeF_2{\cdot}CH_2Cl$, $CMeF_2{\cdot}CHCl_2$, $CMeF_2{\cdot}CCl_3$, m.p. 52·8—53·3°, b.p. 101—102°, $CH_2Cl{\cdot}CF_2{\cdot}CCl_3$, b.p. 150·8—150·9°, $CHCl_2{\cdot}CF_2{\cdot}CCl_3$, and $CF_2(CCl_3)_2$. With 1 : 1 SbF_3–SbF_3Cl_2 at 160° (not under milder conditions), $CH_2Cl{\cdot}CF_2{\cdot}CCl_3$ gives *aay-trichloro-αββ-trifluoro-*, b.p. 108·3°, and *αγ-dichloro-aaββ-tetrafluoro-propane*, b.p. 67·9°. $CH_2Cl{\cdot}CF_2{\cdot}CF_2Cl$ and Cl_2 at room temp. in light give *aay-trichloro-*, b.p. 91·7—91·9°, and *aaay-tetrachloro-*, b.p. 112·0—112·5°, *-ββγγ-tetrafluoro-propane*. R. S. C.

Derivatives of allylic chlorides. Metathesis reactions of methallyl chloride (*iso*butenyl chloride). M. Tamele, C. J. Ott, K. E. Marple, and G. Hearne (*Ind. Eng. Chem.*, 1940, **33**, 115—120; cf. B., 1940, 114).—Commercial methallyl chloride (I), $CH_2{:}CMe{\cdot}CH_2Cl$, contains ~4% of $CMe_2{:}CHCl$, which is unchanged in most reactions not involving the double linking. (I) is hydrolysed by 10% aq. NaOH (or Na_2CO_3) (10% excess) at 110—120° under pressure, with vigorous agitation and control of p_H, to $CH_2{:}CMe{\cdot}CH_2{\cdot}OH$ (II), with ~5% of the ether, which is formed from equimol. amounts of (I) and (II); (II) is stable under the above conditions. Methallyl ethers are obtained from (I)–aq. NaOH–alcohols; rate of etherification depends on the ability of the alcohol to dissociate into $H^{\cdot}$ and OR' ions, and the latter probably react with (I). Physical consts. of Et, b.p. 84·8—86·8°, Pr$^{\beta}$, b.p. 103·8—104·2°, and *sec.*-Bu methallyl ether, b.p. 129·8—130·8°, are recorded. (I) and aq. NH_3 (10 mols.) at 90° give a mixture of $CH_2{:}CMe{\cdot}CH_2{\cdot}NH_2$ (III) (56%), b.p. 78·8°, $(CH_2{:}CMe{\cdot}CH_2)_2NH$ (IV) (26%), b.p. 148—149°, $(CH_2{:}CMe{\cdot}CH_2)_3N$ (8%), b.p. 83—85°/15 mm., and 5% of quaternary amine. (I) (1 mol.), NH_3 (2 mols.), and NH_4Cl (3 mols.) afford 58% of (III) and 10% of (IV). Reaction is rapid in aq. or anhyd. NH_3, but slower in aq. EtOH. (I) and NH_2Ph in aq. Na_2CO_3 at 94° give $CH_2{:}CMe{\cdot}CH_2{\cdot}NHPh$, b.p. 105—106°/10 mm. (84% yield), whilst $(CH_2{\cdot}NH_2)_2$ at 90° yields $(CH_2{:}CMe{\cdot}CH_2{\cdot}NH{\cdot}CH_2)_2$, b.p. 91·8—94·8°/10 mm. (I) and $NHPh_2$ react slowly, if at all. (I) and NaI–COMeEt give $CH_2{:}CMe{\cdot}CH_2I$, b.p. 25—30°/3—5 mm. (12% yield) (decomp. explosively by heat or prolonged storage). (I) and Na_2S at 120°, Na_2S_2 at 120°, or $Na_2S_2O_3$–H_2O or EtOH at 70°, afford the sulphide, b.p. 172·8—173°, disulphide, or mercaptan, b.p. 92·4—92·6°, respectively. (I) and NaCN or, better, CuCN–$PhNO_2$ at 125—130° give $CH_2{:}CMe{\cdot}CH_2{\cdot}CN$, b.p. 136·2—136·4°. (I) and Mg–Et_2O afford $CH_2{:}CMe{\cdot}CH_2{\cdot}MgCl$ (with MeCHO it yields $CH_2{:}CMe{\cdot}CH_2{\cdot}CHMe{\cdot}OH$, b.p. 129°) and thence dimethallyl (V), b.p. 114·3°. (I) and MgBu$^{\alpha}$Cl, Pr$^{\beta}{\cdot}[CH_2]_2{\cdot}MgCl$, MgPhBr, or MgMeBr (in Pr$^{\beta}$$_2$O) afford *β*-methyl-, b.p. 119—121°, or *βζ*-dimethyl-Δ^{α}-heptene, b.p. 140—143°, or $CH_2{:}CMe{\cdot}CH_2Ph$, b.p. 175—176°, or *β*-methyl-Δ^{α}-butene, respectively. (I), Mg, and $COMe_2$ or COMePr$^{\alpha}$ in Et_2O yield $CH_2{:}CMe{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$, b.p. 126°, or $CH_2{:}CMe{\cdot}CH_2{\cdot}CMePr^{\alpha}{\cdot}OH$, b.p. 208—210°, respectively, and (III). Relative reactivities of (I), $CH_2{:}CH{\cdot}CH_2Cl$, $CHMe{:}CH{\cdot}CH_2Cl$, and $CHMe{:}CMe{\cdot}CH_2Cl$ with KI at 20° and NaOEt at 35° or 50° are recorded. A. T. P.

Polymerisation of β-methylallyl alcohol and its lower aliphatic esters. J. D. Ryan and F. B. Shaw, jun. (*J. Amer. Chem. Soc.*, 1940, **62**, 3469).—Boiling $CH_2{:}CMe{\cdot}CH_2{\cdot}OH$ and $(RCO)_2O$ give the *acetate*, b.p. 124°, *propionate*, b.p. 142°, and n-*butyrate*, b.p. 161°. The *formate*, b.p. 103°, is prepared by 85% HCO_2H. The esters and alcohol are only slowly polymerised by catalysts or light; the products are viscous liquids, those obtained by light having the highest mol. wt.

R. S. C.

Preparation of unsaturated higher alcohols. VI. S. Komori (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 337—338B; cf. A., 1939, II, 491).—Reductions of the Et ester of the acid from rice oil at ~335°/80—90 atm. for 2 hr., using 20% of catalyst, are described. Using the Zn–Cr oxide catalyst (not activated with AcOH, but poisoned to some extent by H_2O), addition of KNO_3, NH_4NO_3, $NaNO_3$, NaCl, or Na_2SO_4 has no harmful effect; the yield of unsaturated alcohols (I) is ~80—84%. Catalysts prepared from $Na_2Cr_2O_7$–aq. NH_3–$ZnCl_2$ (or $ZnSO_4$) (giving Zn–Na–Cr oxides) give a reduced yield (62—77%); Ba has a bad effect and a Zn–Cu–Cr oxide catalyst also gives lower yields; Cd, Co, and Fe are effective promoters, giving a yield of ~80% of (I).

A. T. P.

Preparation and properties of acetylenic tertiary carbinols. A. F. Thompson, jun., J. G. Burr, jun., and E. N. Shaw (*J. Amer. Chem. Soc.*, 1941, **63**, 186—188).—Addition of CORR′–Et_2O and C_2H_2 to $CMe_2Et{\cdot}OK$–$CMe_2Et{\cdot}OH$ at 0° and subsequent interaction at room temp. gives 78—90% yields of pure $CH{:}C{\cdot}CRR'{\cdot}OH$ (*A*). $n\text{-}C_5H_{11}{\cdot}C{:}C{\cdot}CMeR{\cdot}OH$ (*B*) are similarly obtained from $CH{:}C{\cdot}C_5H_{11}$-*n* (I) and COMeR at 70°, but are better prepared by adding (I) to MgEtBr in Et_2O, determining the amount (85—90%) of $C_5H_{11}{\cdot}C{:}C{\cdot}MgBr$ formed by measuring the C_2H_6 evolved, and finally adding the calc. amount of COMeR. Addition of (*B*) to Al_2O_3 at 230° gives good yields of $n\text{-}C_5H_{11}{\cdot}C{:}C{\cdot}CR{:}CH_2$, but (*A*) mainly regenerate C_2H_2 and COMeR. $CH{:}C{\cdot}CMeR{\cdot}OH$, in which R = Et, b.p. 118—121°, Pr$^\alpha$, b.p. 138—140°, and C_5H_{11}, b.p. 174—176°, $CH{:}C{\cdot}CEt_2{\cdot}OH$ (II), b.p. 138—140°, $CH{:}C{\cdot}CPr^\beta_2{\cdot}OH$, b.p. 162—164°, 1-acetylenyl*cyclo*hexan-1-ol, b.p. 81—83°/18 mm., (*B*) in which R = Et, b.p. 105—110°/25 mm., Pr$^\alpha$, b.p. 100—105°/15 mm., and amyl, b.p. 138—142°/15 mm., *γ-methylene-*Δ^δ*-decinene*, b.p. 80—82°/30 mm., *δ-methylene-*Δ^ϵ*-undecinene*, b.p. 94—97°/30 mm., and *ζ-methylene-*Δ^η*-tridecinene*, b.p. 148—152°/30 mm., are thus prepared.

R. S. C.

Esters of nitro-alcohols. J. B. Tindall (*Ind. Eng. Chem.*, 1940, **33**, 65—66).—Propionates, butyrates, and *iso*butyrates of all the monohydric nitro-alcohols which can be made by condensing $MeNO_2$, $EtNO_2$, Pr$^\alpha NO_2$, Pr$^\beta NO_2$, Bu$^\alpha NO_2$, or $CHMeEt{\cdot}NO_2$ with CH_2O, MeCHO, EtCHO, Pr$^\alpha$CHO, or Pr$^\beta$CHO, respectively, are prepared. Esters of primary nitro-alcohols are made by refluxing with org. acid, H_2SO_4, and C_6H_6, and the esters are refined without neutralising the mixture with alkali (which causes some decomp. during distillation). Direct esterification of *sec.* alcohols is unsatisfactory; esters are made using acid anhydride and H_2SO_4 at ~60° and distilling at 1—2 mm. The following *propionates*, *butyrates*, and *isobutyrates* are prepared (b.p. at 10 mm. of the three esters in this order are given in parentheses): *β-nitroethyl* (106—108·2°; 114·5—115·8°; 103—107·5°), *β-nitropropyl* (106·8—107°; 115—116°; 105—106°), *β-nitro-α-butyl* (111—112°; 119—119·5°; 113—114°); *β-nitro-β-methylpropyl* (105·5—106·3°; 116·2—117°; 106·5—110°), *β-nitro-α-amyl* (114·5—115·5°; 130—133·5°; 121—122·5°), *β-nitro-β-methyl-α-butyl* (116·7—118°; 125·2—127·5°; 117—121°), *α-nitro-β-propyl* (104—105°; 107·2°; 104·3—104·8°), *γ-nitro-β-butyl* (104—106°; 116—117·3°; 109·4—110°), *γ-nitro-β-amyl* (109·5—111·8°; 119·5—123°; 113·9—116·8°), *γ-nitro-γ-methyl-β-butyl* (109·8—110·5°; 117—118·5°; 106—109°), *γ-nitro-β-hexyl* (116·7—119·2°; 128·2—129°; 117·5—119°), *γ-nitro-γ-methyl-β-amyl* (117·2—119°; 125·8—127·5°; 121·4—123·5°), *α-nitro-β-butyl* (111·5—113°; 122—122·5°; 109·1—111·2°), *β-nitro-γ-amyl* (115·2—115·5°; 121·8—123°; 117—118°), *δ-nitro-γ-hexyl* (116·5—118·2°; 124—124·6°; 120—122·5°), *β-nitro-γ-methyl-γ-amyl* (112—113·4°; 122—123·5°; 120—121·8°), *δ-nitro-γ-heptyl* (125—127·6°; 133·8—136·5°; 125·2—125·6°), *γ-nitro-γ-methyl-δ-hexyl* (122·8—127·5°; 132—133°; 131—132·2°), *α-nitro-β-amyl* (118·3—119°; 128—130·8°; 126—128°), *β-nitro-γ-hexyl* (119·8—121·1°; 133·2—135°; 127·8—129·2°), *γ-nitro-δ-heptyl* (128·5—129°; 136—137·5°; 131·6—133·5°), *β-nitro-β-methyl-γ-hexyl* (124·6—125·8°; 130—132°; 127·7—129·5°), *ε-nitro-δ-octyl* (136—138°; 145—146·2°; 141·2—143°), *γ-nitro-γ-methyl-δ-heptyl* (130·8—133·1°; 142—145·6°; 135—139·8°), *α-nitro-γ-methyl-β-butyl* (121—121·5°; 131—131·7°; 123—124°), *β-nitro-δ-methyl-γ-amyl* (116—120·2°; 128—133°; 121—126·4°), *δ-nitro-β-methyl-γ-hexyl* (120·5—121°; 136·8—138°; 130—134°), *β-nitro-ββδ-dimethyl-γ-amyl* (121·1—125·1°; 133—134·6°; 124·5—127·8°), *δ-nitro-β-methyl-γ-heptyl* (133—134·5°; 143·8—146·4°; 137·1—138·5°), and *δ-nitro-ββδ-dimethyl-γ-hexyl* (131—132°; 141·5—142°; 134·6—137·8°). The esters are unstable at b.p./760 mm., but are fairly stable at ∢150°. B.p. ranges of all products at 760 mm. are given, and also vals. of n_D^{20} and d^{20}.

A. T. P.

Isomeric βγ-epoxypentanes. Extent to which mixtures of diastereoisomerides are formed in reactions of some pentane derivatives. H. J. Lucas, M. J. Schlatter, and R. C. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 22—28).—Configurations assigned below are based on the assumption that the reactions parallel those of the corresponding butane derivatives (A., 1939, II, 401). Mixed Δβ-pentenes (prep. from $CHMePr^\alpha{\cdot}OH$ by aq. H_2SO_4 and diatomaceous earth at 90—110°), b.p. 35·5—35·8°/742 mm., with $Ca(OCl)_2$ in aq. AcOH give with inversion 47·5% of mixed $CHEtCl{\cdot}CHMe{\cdot}OH$, b.p. 64—71°/30 mm., converted by conc., aq. KOH at ~125° into βγ-epoxypentanes (96%), which are readily separated by distillation into *trans-* (I) (75%), b.p. 43·7°/200 mm., 80·2°/748 mm., and *cis*-isomerides (II) (25%), b.p. 48·6°/200 mm., 85·4°/748 mm. In very dil. H_2SO_4 at room temp., (I) gives *dl-erythro-*, b.p. 89°/10 mm. [3 : 5-dinitrobenzoate, m.p. 207° (corr.)], and (II) gives *dl-threo*-pentane-βγ-diol, b.p. 83°/10 mm. [3 : 5-dinitrobenzoate, m.p. 160·5° (corr.)]. The corresponding diacetates, b.p. 85°/10 mm. and 89°/10 mm., respectively, obtained therefrom without inversion by Ac_2O and a trace of H_2SO_4, are converted by HBr at 0° with inversion into *threo-* (III) (93·61% pure), b.p. 94°/50 mm., and *erythro-βγ*-dibromo-*n*-pentane (IV) (91·41% pure), b.p. 91°/50 mm. With 48% HBr at <5°, (I) gives *erythro-* (V), b.p. 59°/10 mm., and (II) gives *threo-*$CHEtBr{\cdot}CHMe{\cdot}OH$ (VI), b.p. 53°/10 mm., which by further reaction yield pure (IV), m.p. −56·0°, and (III), m.p. −32·4°, respectively, obtained also directly from (I) and (II) with isolation of (V) and (VI). With Zn in abs. EtOH at 70°, (V) and (VI) give *trans-*, b.p. 35·48°/744 mm., and *cis-*$CHMe{:}CHEt$, b.p. 36·08°/744 mm., respectively, which with Br give (IV) and (III), respectively. With conc. KOH at 100—110°, (V) and (VI) give (I) and (II), respectively. The purity of (III) and (IV) is best determined by the dielectric const., but a correction is required for mixtures.

R. S. C.

Dienes. Mercuration of $\Delta^{\alpha\gamma}$-butadiene. Synthesis of βγ-dialkoxy-$\Delta^{\alpha\gamma}$-butadienes. J. R. Johnson, W. H. Jobling, and G. W. Bodamer (*J. Amer. Chem. Soc.*, 1941, **63**, 131—135).—$(CH_2{:}CH)_2$ and $Hg(OAc)_2$ in abs. EtOH at room temp. or, better, ~75° give meso- (60%), m.p. 162—163°, and dl-*βγ-diethoxy-*αδ*-diacetoxymercuributane* (33—38%), m.p. 111—112°, converted by aq. KI into the HgI_2-compounds, which with I in boiling CCl_4 give 80—85% of meso- (I), m.p. 52—53°, and dl-*αδ-di-iodo-βγ-diethoxybutane* (II), m.p. 46—47°, and thence, in both cases, by aq. NaOH *βγ-diethoxy-*$\Delta^{\alpha\gamma}$*-butadiene* (III), m.p. 32°, b.p. 162—163°/740 mm. Configurations are based on dipole moments: (I) 1·70, (II) 2·20. (III) is hydrolysed by dil. HCl to Ac_2, and with 1 : 4-naphthaquinone in boiling C_6H_6 or with toluquinone at the b.p. gives 2 : 3-diethoxyanthraquinone, m.p. 167—168° (lit. 160—163°), and 6 : 7-*diethoxy-2-methyl-*1 : 4*-naphthaquinone*, m.p. 132—133° (corr.), respectively. $(CH_2{:}CH)_2$ and $Hg(OAc)_2$ in boiling MeOH afford similarly *meso-* (70%), m.p. 130—135°, and *dl-*$(OMe{\cdot}CH{\cdot}CH_2{\cdot}Hg{\cdot}OAc)_2$ (17%), m.p. 148—149°, and thence meso-, m.p. 99—100°, and dl-*αδ-di-iodo-βγ-dimethoxybutane*, m.p. 37—38°, *αδ-dibromo-βγ-dimethoxybutane*, m.p. 83—84°, *βγ-dimethoxy-*$\Delta^{\alpha\gamma}$*-butadiene*, m.p. 19°, b.p. 134·5—135·5°/745 mm., 51—52°/30 mm., and 2 : 3-dimethoxyanthraquinone, m.p. 231—233° (lit. 235—236°, 237°).

R. S. C.

Cleavage of isomerides of hexosemonophosphoric acid by phosphatase.—See A., 1941, III, 137.

Vinyl polymerides. X. Polymerides of α-halogenoacrylic acids and their derivatives. C. S. Marvel, J. Dec, H. G. Cooke, jun., and J. C. Cowan. **XI. Optically active polymerides from active vinyl esters. Method of studying the kinetics of polymerisation.** C. S. Marvel, J. Dec, and H. G. Cooke, jun. (*J. Amer. Chem. Soc.*, 1940, **62**, 3495—3498, 3499—3504; cf. A., 1941, II, 3).—X. $CH_2X{\cdot}CHX{\cdot}CO_2Me$

(X = Cl, b.p. 72—75°/21 mm., or Br, b.p. 96—98°/22 mm.), prepared from CH_2:CH·CO_2Me by Cl_2 or Br in MeOH at <40°, is hydrolysed by boiling 20% HCl or HBr to CH_2X·CHX·CO_2H (X = Cl, m.p. 49—50°, b.p. 130—133°/26 mm., or Br, m.p. 59—60°), which with $SOCl_2$ gives the chloride (*A*) (X = Cl, b.p. 52—54°/16 mm., or Br, b.p. 81—84°/18 mm.). Heating (*A*) with the appropriate alcohol at 100° gives sec.-*Bu*, b.p. 65—66°/25 mm., cyclo*hexyl*, b.p. 95—97°/2 mm., and *β*-*chloroethyl* *αβ*-*dichloropropionate*, b.p. 123—126°/22 mm., and sec.-*Bu*, b.p. 130—135°/26 mm., and cyclo*hexyl* *αβ*-*dibromopropionate*, b.p. 130—132°/2 mm. *Ph* *αβ*-*dichloro*-, b.p. 130—135°/18 mm., and *αβ*-*dibromo*-*propionate*, b.p. 132—133°/2 mm., are prepared by adding C_5H_5N (1) to (*A*) (1) and PhOH (1 mol.) in C_6H_6 at >20° and keeping overnight at 5°. In quinoline–, quinaldine–, or NPhMe$_2$–N_2 at 100° CH_2X·CHX·CO_2R give *Et*, b.p. 51—53°/18 mm., sec.-*Bu*, b.p. 73—73·5°/23 mm., cyclo*hexyl*, b.p. 51—53°/2 mm., *Ph*, b.p. 91—93°/8 mm., and CH_2Cl·CH_2 *α*-*chloroacrylate*, b.p. 94—96°/20 mm., sec.-*Bu*, b.p. 80—82°/23 mm., cyclo*hexyl*, b.p. 100—106°/4 mm., and *Ph* *α*-*bromo*-*acrylate*, b.p. 95—96°/2 mm. When kept alone or in solution, the α-halogenoacrylates give head-to-tail polymerides, readily in ultra-violet light, when heated, or when treated with Bz_2O_2. *Polymerides*, [·CH_2·CHX(CO_2R)·]$_n$, (*a*) X = Cl, R = Et, decomp. 160—170°, *sec.*-Bu, decomp. 160—165°, *cyclo*hexyl, decomp. 210—235°, Ph, decomp. 160—168°, CH_2Cl·CH_2 (soft), decomp. 230—240°, and (*b*) X = Br, R = Et, decomp. 125—130°, *sec.*-Bu, decomp. 150—160°, *cyclo*-hexyl, decomp. 140—150°, Ph, decomp. 175—185°, are described. When prepared in absence of a solvent, they are usually hard, clear glasses, *n* 1·5—1·6. When prepared in dioxan (**I**) they are pptd. by Et_2O or EtOH. Some lactone is also formed, particularly when polymerisation is effected slowly in (**I**). The Cl-polymerides are mostly stable in light, the Br-polymerides less stable. CH_2:CBr·CO_2H, m.p. 71—72°, prepared (70%) from CH_2Br·CHBr·CO_2Me by boiling aq. Ba(OH)$_2$, gives a polymeride which rapidly decomposes to give a Br-free product. CH_2:CCl·CO_2H, m.p. 64—65°, similarly prepared, with Bz_2O_2 at 70° or in EtOH in light gives a H_2O-sol. polymeride, but in boiling H_2O gives a cross-linked lactone. CH_2:CCl·COCl [prep. from (*A*) by NPhEt$_2$ at 85°] gives a H_2O-sol. polymeride. Polymerised CH_2:CBr·CO_2H is unstable.

XI. Formation of polymerides, $[\alpha]_D^{30}$ +7·4° in (**I**) and $[\alpha]_D^{25}$ −29·1° in (**I**), from d-sec.-*Bu* *α*-*chloroacrylate* (**II**), b.p. 70—71°/23 mm., $[\alpha]_D^{25}$ +26·0° in (**I**), and *vinyl* l-*β*-*phenylbutyrate* (**III**), b.p. 96—98°/2 mm., $[\alpha]_D^{25}$ −20·4° in (**I**), is shown to be bimol. by the rate of change of *α*. (**II**) is obtained by the method given above. (**III**) is obtained from CHPhMe·CH_2·CO_2H (prep. from CHMe:CH_2·CO_2H by $AlCl_3$–C_6H_6 in 89% yield) by C_2H_2, $Hg_3(PO_4)_2$, and a trace of quinol at 100°, but is accompanied by 3-methylindanone (**IV**) (2 : 4-*dinitrophenylhydrazone*, m.p. 239—241°). (**III**) and (**IV**) form a const.-boiling mixture, but (**IV**) is separated by Girard's reagent. *Vinyl* dl-*β*-*phenylbutyrate*, b.p. 93—94°/2—3 mm., is also prepared. R. S. C.

Equilibria between esters, hydrogen, and alcohols. R. Burks, jun., and H. Adkins (*J. Amer. Chem. Soc.*, 1940, **60**, 3300—3302).—Hydrogenation of aliphatic dicarboxylic esters to glycols in presence of Cu chromite at 240—260° is a reversible reaction. The amount of ester at equilibrium is always <1%, being greater at lower temp. and lower pressures. Purification of OH·[CH_2]$_6$·OH, thus obtained, is improved. R. S. C.

Photochemical decomposition of malonic acid.—See A., 1941, I, 122.

α-Hydroxy-ββ-dimethyl-γ-butyrolactone. H. E. Carter and L. F. Ney (*J. Amer. Chem. Soc.*, 1941, **63**, 312—313).—OH·CH_2·CMe_2·CHO, $CaCl_2$, and KCN in H_2O, first at room temp. and later at 70—80°, give 77—81% of α-hydroxy-ββ-dimethyl-γ-butyrolactone. R. S. C.

Introduction of substituted vinyl groups. VI. Regeneration of substituted vinylmalonic esters from their sodium enolates. A. C. Cope and (Miss) E. M. Hardy (*J. Amer. Chem. Soc.*, 1940, **62**, 3319—3323; cf. A., 1940, II, 152).—Treating the enolates (prep. by $NaNH_2$) of Et_2 *iso*propylidene-, b.p. 111—113°/9 mm., α-methyl*iso*propylidene-, b.p. 119·5—120·5°/10 mm., and *cyclo*pentylidene-malonate, b.p. 142—143°/10 mm., in Et_2O with aq. HCl, solid BzOH, AcOH, or H_2O gives CHMe:CH·CH(CO_2Et)$_2$ (**I**), b.p. 105—106°/12 mm. (corresponding *di*-p-*nitrobenzyl* ester, m.p. 119·5—120·5°), Et_2 *α*-*methylpropenyl*- (**II**), b.p. 116—117°/10 mm. (with O_3 gives MeCHO), and 1-cyclo*pentenyl*-*malonate* (**III**), b.p. 147—148°/17 mm., respectively. In presence of Raney Ni–N_2 at 180°, (**I**), (**II**), and (**III**) give 98, 86, and 63%, respectively, of the αβ-unsaturated esters. Analysis of the mixtures by ICl is unsatisfactory but is readily achieved by polarographic analysis (only the αβ-unsaturated esters being reduced), which is checked by determination of *n*. R. S. C.

Reduction of substituted malonates. A. H. Bhatkhande, N. L. Phalnikar, and B. V. Bhide (*J. Univ. Bombay*, 1940, **9**, Part 3, 170—171).—Reduction (Na + EtOH) of $CPr_2(CO_2Et)_2$ yields 35% of $CHPr_2$·CH_2·OH. A. Li.

Sodium hydrogen dimethylmaleate. M. Couper, C. J. Kibler, and R. E. Lutz (*J. Amer. Chem. Soc.*, 1941, **63**, 2—3).—Dissolution of (:CMe·CO)$_2$O (**I**) (1 mol.) in aq. NaOH (2 mols.) and addition of 1 mol. of HCl thereto ppts. *Na H dimethylmaleate* (**II**), which can be recrystallised from aq. EtOH, but in warm H_2O or in cold acid gives (**I**) and (:CMe·CO_2Na)$_2$. With aq. NaOH at 188°, (**I**) gives dimethyl-fumaric (37%) and methylitaconic acid (12%) and (**I**) [37%; separated mainly as (**II**)]. R. S. C.

Photolysis of acetaldehyde.—See A., 1941, I, 121.

Free radicals in the photolysis of propaldehyde.—See A., 1941, I, 122.

Condensation of ketones by aluminium *tert.*-butoxide to compounds of the mesityl oxide type. W. Wayne and H. Adkins (*J. Amer. Chem. Soc.*, 1940, **62**, 3401—3404).—Al(OBu$^\gamma$)$_3$ at 60—140° is usually superior to other reagents for condensation of COMeR to dimeric products of mesityl oxide type. It is usually advantageous to remove Bu$^\gamma$OH as formed and to raise the temp. as reaction proceeds. Xylene is often a useful solvent. 1 mol. of Al(OBu$^\gamma$)$_3$ is used for 2 mols. of ketone. Yields are: R = Et, Bu$^\alpha$, Bu$^\beta$, or Ph 70—80%; R = Pr$^\beta$ 49, CH_2Bu$^\gamma$ 36, Bu$^\gamma$ 10%; α-hydrindone 48%; *cyclo*hexanone 78%; $COEt_2$ 21%; COPhEt 21%; $COPr^\alpha_2$, $COPr^\beta_2$, and $COBu^\beta_2$ 0. $COMe_2$ gives 37% of CMe_2:CH·COMe and 19% of phorone. Phorone gives 21% of (?) dimeride, b.p. 104—110°/1 mm. The following are prepared, the ethylenic linking being probably mainly but not entirely contiguous to CO. *ββδθ-Trimethyl*-Δ$^\delta$-*nonen*-ζ-*one*, b.p. 86—90°/8 mm. COEt·CH:CMeEt, b.p. 82—86°/42 mm. *βγζ-Trimethyl*-Δ$^\gamma$-*hepten*-ε-*one*, b.p. 100—104°/45 mm. ε-*Methyl*-Δ$^\epsilon$-*undecen*-η-*one*, b.p. 99—104°/8 mm. *ββγζθ-Penta-methyl*-Δ$^\gamma$-*hepten*-ε-*one*, b.p. 74—76°/8 mm. *ββδδθθ-Penta-methyl*-Δ$^\delta$-*nonen*-ζ-*one*, b.p. 102—106°/8 mm. 2-*cyclo*Hexyl-idene*cyclo*hexan-1-one, b.p. 123—126°/8 mm. α-Anhydro-bishydrindone, m.p. 142—144°. *α-Methyl-β-ethylchalkone*, b.p. 135—140°/1 mm. δ-*Methyl*-γ-*ethyl*-Δ$^\gamma$-*hepten*-ε-*one*, b.p. 101—104°/44 mm. R. S. C.

Acyclic derivatives of *d*-lyxose. M. L. Wolfrom and F. B. Moody (*J. Amer. Chem. Soc.*, 1940, **62**, 3465—3466).—*d*-Lyxose with EtSH in conc. HCl at 0° gives the H_2O-sol. *Et$_2$ mercaptal*, m.p. 103—104°, $[\alpha]_D^{24}$ +41° in H_2O [*tetra-acetate* (**I**), m.p. 36—37°, $[\alpha]_D^{28}$ +40·5° in $CHCl_3$], converted by $HgCl_2$–$CdCO_3$ in moist $COMe_2$ into a syrupy *aldehydo*-compound, which with Ac_2O–C_5H_5N at room temp. gives *aldehydo*-d-*lyxose hexa-acetate*, m.p. 87—88°, $[\alpha]_D^{20}$ +13° in $CHCl_3$, obtained also from (**I**) by H_2SO_4–Ac_2O at room temp. Attempts to prepare other *aldehydo*-derivatives yielded syrups. R. S. C.

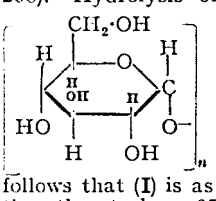
Structure of γ-sugars. V. Conclusions. F. Hartley and W. H. Linnell (*Quart. J. Pharm.*, 1940, **13**, 332—343; cf. A., 1940, II, 323).—The absence of mutarotation in 6-methyl- (**I**), 3 : 4 : 6-trimethyl- (**II**), and 1 : 3 : 4 : 6-tetramethyl-fructose (**III**), and 5-methylglucose precludes a cyclic structure for these substances. The action of BzO_2H and O_3 on (**I**), (**II**), (**III**), and their methylfructosides indicates the absence of olefinic linkings and excludes an enediol structure for these substances. A keto-alcohol structure is assigned to γ-fructose and its non-glycosidic derivatives, an aldehyde-alcohol structure to γ-glucose and its non-glycosidic derivatives, and a furanose ring structure to γ-glucosides; this affords an explanation of the difference in stability between γ-sugars and their glycosides. Hydrolysis of α-methylgluco-furanoside and -pyranoside by 0·1N-HCl gives activation energies of 16,055 and 17,590 g.-cal. per g.-mol., respectively. The greater ease of acid-hydrolysis of furanosides compared with pyranosides is discussed. F. O. H.

Action of diazomethane on acyclic sugar derivatives. I. M. L. Wolfrom, D. I. Weisblat, W. H. Zophy, and S. W. Waisbrot (*J. Amer. Chem. Soc.*, 1941, **63**, 201—203).—d-*Arabinose Et₂ mercaptal*, m.p. 125—126°, $[\alpha]$ 0° in C_5H_5N, gives the *tetra-acetate*, m.p. 80°, $[\alpha]_D^{23}$ +30° in $CHCl_3$, which with $HgCl_2$–$CdCO_3$ in $COMe_2$ gives aldehydo-d-*arabinose tetra-acetate* (**I**), m.p. 113—115°, $[\alpha]_D^{23}$ +65° in $CHCl_3$ (*semicarbazone*, m.p. 183—185°, $[\alpha]_D^{30}$ −72·0° in $CHCl_3$). With CH_2N_2 in Et_2O–$CHCl_3$ at 0—5°, this gives l-*deoxy*-keto-d-*fructose tetra-acetate* (**II**) (62%), m.p. 75—77°, $[\alpha]_D^{31}$ +55·5° in $CHCl_3$, $[\alpha]_D^{22}$ +58·3° (stable) in MeOH (*oxime*, m.p. 112—113°, $[\alpha]_D^{33}$ +8·7° in $CHCl_3$), and a substance, m.p. 162—164° (decomp.), $[\alpha]$ +41° in $CHCl_3$. The *l*-isomeride of (**I**) similarly gives the l-*isomeride*, m.p. 77—78°, $[\alpha]_D^{25}$ +(?−)55° in $CHCl_3$, of (**II**) and a substance, m.p. 162—164° (decomp.), $[\alpha]_D^{23}$ −41° in $CHCl_3$. The dl-*form*, m.p. 95—97°, α 0 in $CHCl_3$, of (**II**) is prepared by crystallising a 1 : 1 mixture of the *d*- and *l*-forms. CHI_3 is formed from (**II**) by NaOH–KI_3 in aq. dioxan. *d*-Gluconyl chloride penta-acetate and CH_2N_2 in Et_2O at room temp. give 1-*diazo*-1-*deoxy*-keto-d-*glucoheptulose penta-acetate* (**III**), m.p. 106—106·5°, $[\alpha]_D^{30}$ +65·8° in $CHCl_3$, and a substance, m.p. 86°, containing Cl. Fehling's solution is reduced by (**II**) and (**III**). (**II**) gives Selivanov's ketose reaction.

R. S. C.

Muscadinin hydrochloride, $C_{22}H_{33}O_{17}Cl$, +2·5H_2O, sinters at 181° (corr.), m.p. 184° (decomp.).—See A., 1941, III, 151.

Molecular constitution of an insoluble polysaccharide from yeast, *Saccharomyces cerevisiæ*. W. Z. Hassid, M. A. Joslyn, and R. M. McCready (*J. Amer. Chem. Soc.*, 1941, **63**, 295—298).—Hydrolysis of the polysaccharide (**I**) from bakers' yeast causes upward mutarotation. Ac_2O and a little Cl_2 at room temp. and later 80° give an *acetate*, $[C_6H_7O_5(OAc)_3]_n$, $[\alpha]_D$ −72°. Me_2SO_4–aq. NaOH–CCl_4 gives an *ether*, $[C_6H_7O_5(OMe)_3]_n$, $[\alpha]_D$ +4·5° in $CHCl_3$, hydrolysed by HCl–MeOH to 2 : 4 : 6-trimethylmethylglucoside only. It follows that (**I**) is as shown. Since η shows the mol. wt. of the ether to be ~6500, non-formation of a tetramethylglucoside indicates that the mol. is probably a closed loop of such units.



R. S. C.

Polysaccharides of the phosphatide obtained from cell residues for the preparation of tuberculin.—See A., 1941, III, 144.

ε-Galactan of larch wood. E. L. Hirst, J. K. N. Jones, and W. G. Campbell (*Nature*, 1941, **147**, 25—26).—Investigation of the hydrolysis products obtained from methylated ε-galactan (**I**) supports the view (A., 1940, II, 365) that (**I**) is a mixture of a galactan and an araban. On hydrolysis, the methylated (**I**) gives 2 : 3 : 4 : 6-tetra-, 2 : 4-di-, tri-methyl-galactopyranose (1 : 1 : 1 mol.), and a small amount of a methylated uronic acid. The general type of structure of (**I**) is outlined.

L. S. T.

Constitution of amylopectin. K. H. Meyer and H. P. Bernfeld (*Arch. Sci. phys. nat.*, 1940, [v], **22**, *Suppl.*, 92—95).—Starch is dissolved at 60—80° by CCl_3·CHO, CCl_3·CO_2K, and $CS(NH_2)_2$; at a lower temp. it swells and when heated suddenly dissolves, which is evidence of the presence of weak reticular linkings. Amylopectin is degraded by β-amylase to a dextrin, whereas after the prior action of α-amylase, the action of the β-form results in complete breakdown. Thus the branching chains probably form 1 : 6-linkings and are not those visualised by Hirst and Young (cf. A., 1939, II, 495).

J. L. D.

Specificity of choline-esterase. D. Glick (*J. Biol. Chem.*, 1941, **137**, 357—362; cf. A., 1939, III, 1096).—*β-Bromoethyl-valerate*, b.p. 112—114°/25 mm., *hexoate*, b.p. 124—126°/23 mm., *heptoate*, b.p. 138—140°/24 mm., *succinate*, b.p. 216—217°/26 mm., and *maleate*, m.p. 66°, and NMe_3 give the corresponding *choline bromide esters*, the m.p. of the *platinichlorides* of which are respectively, 211°, 204—206°, 198—200°, 222° (decomp.), and 230° (decomp.). Enzymic hydrolysis of the *n*-acylcholine esters increases with lengthening of the C chain to the butyryl compound, and then decreases. The dicarboxylic esters are hydrolysed relatively slowly and succinyl- is hydrolysed more slowly than is maleyl-choline. There is no relation between the rates of hydrolysis of *n*-acyl esters of choline from Ac to valeryl inclusive and their biological effects.

J. N. A.

β-Dialkylaminoethyl bromide hydrobromides and β-dialkylaminoethylamines. L. H. Amundsen and K. W. Krantz (*J. Amer. Chem. Soc.*, 1941, **63**, 305—307).—OH·$[CH_2]_2$·NR_2 and HBr give *β-di-methyl-*, m.p. 188·5—189·9° (decomp.), *-ethyl-*, m.p. 208·1—208·4° (decomp.), *-n-propyl-*, m.p. 159·6—160·1° (slight decomp.), and *-n-butyl-*, m.p. 85·7—85·9°, *-aminoethyl bromide hydrobromide*, which with NH_3–EtOH at room temp. give a little (>5%), 28, 34, and 46%, respectively, of *NN*-dimethyl- (*α-naphthylcarbamide*, m.p. 148·6—148·8°), *-ethyl-*, b.p. 79—82°/85 mm. (*α-naphthylcarbamide*, m.p. 103·7—103·9°), *-n-propyl-*, b.p. 87—88°/30 mm. (*α-naphthylcarbamide*, m.p. 115·7—116·2°), and *-n-butyl-*, b.p. 98—101°/13 mm. [*α-naphthylcarbamide*, m.p. 101·1—101·6° (decomp. from 93°)], *-ethylenediamine*. M.p. are corr.

R. S. C.

Identity of α- and β-earleine with betaine and choline, respectively. A. Stempel and R. C. Elderfield (*J. Amer. Chem. Soc.*, 1941, **63**, 315—316).—Identities as named are established (cf. A., 1940, II, 185).

R. S. C.

Methylation of hexosamines. P. A. Levene (*J. Biol. Chem.*, 1940, **137**, 29—39).—Methylation (Me_2SO_4) of glucosamine and chondrosamine penta-acetates in MeOH–CCl_4 yields *N*-acetyltrimethylmethyl-glucosaminide, m.p. 190°, $[\alpha]_D^{25}$ +20° in $CHCl_3$, 0° in MeOH or $COMe_2$ (Cutler *et al.*, A., 1938, II, 46), and *-chondrosaminide* (**I**), m.p. 223°, $[\alpha]_D^{25}$ −12·5° in $(CHCl_2)_2$ [with a form, $[\alpha]_D^{25}$ +111·4° in $(CHCl_2)_2$], reduced ($SnCl_2$ + HCl) to trimethyl-glucosamine and *-chondrosamine hydrochloride*, m.p. 198°, $[\alpha]_D^{25}$ +152·5° (initial), 105° (equilibrium in H_2O), and oxidised by HgO to *trimethyl-glucosamic*, m.p. 178—179°, $[\alpha]_D^{25}$ +10·5° in MeOH, and *-chondrosamic acid*, m.p. 187°, $[\alpha]_D^{25}$ +7·0° in MeOH, or by chloramine-*T* to 2 : 3 : 5-trimethyl-arabinose and -lyxose respectively. (**I**) therefore has the pyranoside structure. It is hydrolysed (MeOH–HCl) to *trimethylmethylchondrosaminide*, m.p. 227°, $[\alpha]_D^{25}$ +150·3° in MeOH.

A. Lt.

***d*-Glucamine from *d*-glucose.** W. Wayne and H. Adkins (*J. Amer. Chem. Soc.*, 1940, **62**, 3314—3316).—Glucosamine is prepared in 26% yield (as CHPh: derivative) from glucose or glucoscimine (**I**) by H_2–NH_3–Raney Ni in MeOH at 100—115°/155 atm. or in 15% yield similarly from glucoseoxime. Attempts to prepare (**I**) by Muskat's method (A., 1934, 512) give a hygroscopic product, m.p. 49—51°, $[\alpha]_D^{25}$ +26·1°→+20·9° in 24 hr. in H_2O.

R. S. C.

Enzymic decomposition of glucosamine.—See A., 1941, III, 138.

Action of periodic acid on glucosamine derivatives. A. Neuberger (*J.C.S.*, 1941, 47—50).—Et 4 : 6-benzylideneglucosamate hydrochloride with BzCl and $NaHCO_3$ yields *Et N-benzoyl-4 : 6-benzylideneglucosamate*, m.p. 173—174°, $[\alpha]_D$ −80° in $CHCl_3$, which with H_2–Pd gives *Et* N-*benzoylglucosamate*, m.p. 144—145°, $[\alpha]_D$ +11·8° in H_2O, completely decomposed by $Pb(OAc)_4$ with absorption of 4·5 mols. of O_2 per mol., or by HIO_4 or $NaIO_4$. *N*-Methylglucosamic acid reacts with only 2 mols. of HIO_4 giving CH_2O and (?) HCO_2H, but no NH_3 or I. *N*-Acetyl- or *-benzoyl-α-methylglucosaminide*, m.p. 225—226°, $[\alpha]_D$ +114° in H_2O (from *N*-benzoylglucosamine tetra-acetate and 2·1% MeOH–HCl), with HIO_4 absorbs 2 equivs. of O_2, whilst the former with $NaIO_4$ absorbs only 1 atom per mol. *N*-Acetyl-3-methyl-α-methylglucosaminide is unaffected by HIO_4 or $NaIO_4$.

A. Lt.

Preparation of 3-methylglucosamine. A. Neuberger (*J.C.S.*, 1941, 50—51).—*N*-Acetyl-α-methylglucosaminide with PhCHO and $ZnCl_2$ yields the 4 : 6-*CHPh:* derivative, m.p. 255°, $[\alpha]_D$ +19° in $CHCl_3$, methylated (Me_2SO_4 in dioxan) to the 3-*Me* compound, m.p. 277—279°, $[\alpha]_D$ +39° in $CHCl_3$, hydrolysed (60% AcOH) to *N-acetyl-3-methyl-α-methylglucosaminide*, m.p. 211°, $[\alpha]_D$ +116° in H_2O. Further hydrolysis (dil. HCl) of this yields *3-methylglucosamine hydrochloride*, m.p. 215° (decomp.), $[\alpha]_D$ +123° (initial, in H_2O), +91·3° (18 hr.), oxidised (HgO) to 3-methylglucosamic acid.

A. Lt.

Allylacetyl-β-alanine, m.p. 70°, and γδ-dihydroxyvaleryl-β-alanine Me ester, m.p. 48—49°, b.p. 80—90°/10^{-5} mm.—See A., 1941, III, 117.

Separation of higher monoamino-acids by countercurrent liquid–liquid extraction: amino-acid composition of wool. A. J. P. Martin and R. L. M. Synge (*Biochem. J.*, 1941, **35**, 91—121).—The literature on countercurrent liquid–liquid extraction is reviewed and the mathematical and physical bases of the separation of *N*-acylamino-acids by liquid–liquid extraction are discussed. A forty-unit $CHCl_3$–H_2O

countercurrent extraction train, its mode of operation, and its application to the determination of a known mixture of NH_2-acids as their *N*-Ac derivatives are described. Using a mixture of *N*-acetyl-methionine, -valine, -proline, -phenylalanine, and -leucine, the substances are recovered in ~95% yield. The NH_2-acid composition of the hydrolysate from wool is determined by this method and the results are compared with those obtained by other methods. The amount of protein required is 10 g. Moreover the residues from the first extraction can be used for the isolation of hydroxyamino-acids by the process of acetylation–benzoylation (A., 1940, II, 38). The data for the partition coeff. of several *N*-acetamido-acids between $CHCl_3$ and water given by Synge (*ibid.*, 37) are redetermined and supplemented. J. N. A.

Carbon suboxide and proteins. I. Nature of the reaction. II. Determination of malonic acid. W. F. Ross and H. N. Christensen. **III. Reaction of carbon suboxide with amino-acids.** W. F. Ross and L. S. Green (*J. Biol. Chem.*, 1940, **137**, 89—99, 101—104, 105—111).—I. With C_3O_2 at 0°, and p_H 8·5, glycine in H_2O yields *malonyldiglycine*, m.p. 236°, also obtained by hydrolysing the Et_2 ester (Pauw, A., 1936, 711). Malonyl compounds are similarly prepared from ovalbumin, chymotrypsin, and serum-albumin. Determination of lysine and $CH_2(CO_2H)_2$ and electrometric titration of the last product show that each free NH_2 combines with one malonyl group.

II. $CH_2(CO_2H)_2$ (free and combined) in malonyl-proteins is determined by hydrolysis and titration with $Ce(SO_4)_2$ before and after heating at 140° in acid solution.

III. With C_3O_2 in H_2O at p_H 8·0 or 8·5, ε-benzoyl-*dl*-lysine yields *malondi-(ε-benzoyl-*dl*-lysine)-α-amide*, decomp. 239—240°. *α-Benzoyl-*l*-lysine*, m.p. 250° (sintering), $[\alpha]^{25}$ +21·6° in H_2O containing 1 equiv. of NaOH [prepared by hydrogenating (Pd) *α-benzoyl-ε-carbobenzyloxy-*l*-lysine*, m.p. 107° (from ε-carbobenzyloxy-*l*-lysine)], yields *malondi-(α-benzoyl-*l*-lysine)-ε-amide*, m.p. 267—268°, and *N*-carbobenzyloxy-*l*-tyrosine (**I**) yields *di-* (90·5%), m.p. 135° (decomp.) [*Me* ester, m.p. 145° (decomp.)], and *mono-(N-carbobenzyloxy-*l*-tyrosyl) malonate* (2·4%), m.p. 53° [also synthesised from (**I**), $CO_2H{\cdot}CH_2{\cdot}COCl$, and NaOH at 0°]. The significance of these reactions is discussed. Arginine, histidine, and serine do not react. Aq. NH_3 with excess of C_3O_2 at 0° yields $CH_2(CO{\cdot}NH_2)_2$. A. Li.

Acylthiocarbamides. M. L. Moore and F. S. Crossley (*J. Amer. Chem. Soc.*, 1940, **62**, 3273—3274).—$CS(NH_2)_2$ and RCOCl in boiling PhMe give 34—68% of *N*-acetyl-, m.p. 165°, N-*propionyl-*, m.p. 148°, *-valeryl-*, m.p. 139°, *-hexoyl-*, m.p. 138°, *-heptoyl-*, m.p. 133°, *-octoyl-*, m.p. 138°, *-undecoyl-*, m.p. 136·5°, *-iso*butyryl-, m.p. 114·5°, *-iso*valeryl-, m.p. 157·5°, -iso*hexoyl-*, m.p. 155°, and *-δ-methyl-α-ethyl-*n*-hexoyl-*, m.p. 89·5°, *-thiocarbamide*. N-*Acetyl-*, m.p. 170·5°, *-propionyl-*, m.p. 127·5°, *-valeryl-*, m.p. 93°, *-hexoyl-*, m.p. 85°, *-heptoyl-*, m.p. 76°, *-octoyl-*, m.p. 81·5°, *-undecoyl-*, m.p. 80·5°, -iso*butyryl-*, m.p. 121·5°, -iso*valeryl-*, m.p. 156°, and -iso*hexoyl-*, m.p. 78·5°, *-N-methylthiocarbamide* are also prepared. Condensation in $COMe_2$ at room temp. gives the *S*-acylthiocarbamide hydrochlorides, which lose HCl and rearrange in boiling PhMe. The *N*-acyl compounds are relatively ineffective as hypnotics. R. S. C.

Photolysis of organic nitrogen compounds.—See A., 1941, I, 122.

Preparation of "silicononyl alcohol." E. L. Niedzielski (*J. Amer. Chem. Soc.*, 1940, **62**, 3519).—$SiEt_3{\cdot}[CH_2]_2{\cdot}Cl$ (prep. from $SiEt_4$), KOAc, and AcOH give 28% of $SiEt_3{\cdot}[CH_2]_2{\cdot}OAc$, b.p. 208—214°, hydrolysed by 22% KOH–EtOH to $SiEt_3{\cdot}[CH_2]_2{\cdot}OH$ (48%), b.p. 190°. R. S. C.

Metallo borohydrides.—See A., 1941, I, 123.

Metallo-organic compounds. VIII. Tin trimethyl oxide and tin trimethyl hydroxide. T. Harada (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1940, **38**, 115—117).—*Sn Me_3 oxide*, b.p. 84°/22 mm. (from $SnMe_3{\cdot}OH$ and Na in C_6H_6) (cf. Kraus *et al.*, A., 1925, i, 1253), yields with H_2O, $SnMe_3{\cdot}OH$, and with $SnMe_3$ halide, $(SnMe_3)_3OX$. A. Li.

II.—HOMOCYCLIC.

Common basis of intramolecular rearrangements. VII. Inapplicability of a free radical mechanism. Formation of 1 : 1-dimethyl*cyclo*propane and neopentane by the action of sodium on neopentyl chloride. Relation to the mechanism of the Wurtz reaction. F. C. Whitmore, A. H. Popkin, H. I. Bernstein, and J. P. Wilkins (*J. Amer. Chem. Soc.*, 1941, **63**, 124—127; cf. A., 1939, II, 353).—1 mol. of $CH_2Bu^{\gamma}Cl$ with 1 atom of Na gives exothermally 36% of CMe_4, 25% of 1 : 1-dimethyl*cyclo*propane (**I**), and 13% of $(CH_2Bu^{\gamma})_2$ (cf. A., 1939, II, 400), but with 0·2 atom of Na gives 41% of CMe_4, 51% of (**I**), and 1·4% of $(CH_2Bu^{\gamma})_2$. This confirms the view that the Wurtz reaction, but not rearrangement of CH_2Bu^{γ} to CMe_2Et, involves free radicals. *iso*-$C_5H_{11}Cl$ and KOH–EtOH give 18% of $CH_2{:}CHPr^{\beta}$, b.p. 18·8°/731 mm., and much *iso*-$C_5H_{11}{\cdot}OEt$. $Pr^{\beta}CHO$, 40% CH_2O, and KOH in EtOH, first at room temp. and then at the b.p., give 50% of $CMe_2(CH_2{\cdot}OH)_2$, m.p. 126—128°, converted by PBr_3 into $CMe_2(CH_2Br)_2$ (34·6%), b.p. 84°/28 mm., which with Zn dust, NaI, Na_2CO_3, and NH_2Ac at 150—165° gives (**I**), m.p. −108·4° to −107·3°, b.p. (calc.) 19·9°. (**I**) is differentiated from $CH_2{:}CHPr^{\beta}$ by solubility in 66% H_2SO_4 at 0° and failure to react with O_3, $KMnO_4$, or Br–CCl_4. R. S. C.

Action of anhydrous ferric chloride on alkylbenzenes. (Miss) D. Nightingale, R. G. Taylor, and H. W. Smelser (*J. Amer. Chem. Soc.*, 1941, **63**, 258—261).—$FeCl_3$ rearranges 1 : 3 : 4-$C_6H_3Me_2Bu^{\alpha}$ at 80—110° to 1 : 3 : 5-$C_6H_3Me_2Bu^{\beta}$, and 1 : 3 : 4-$C_6H_3Me_2{\cdot}CHMeEt$ or -$C_6H_3Me_2Bu^{\gamma}$ at 80° or -$C_6H_3Me_2Bu^{\beta}$ at 80—100° to 1 : 3 : 5-$C_6H_3Me_2Bu^{\gamma}$. It is without effect on 1 : 3 : 4-$C_6H_3Me_2Pr^{\alpha}$, -$C_6H_3Me_2Pr^{\beta}$, or -$C_6H_3Me_2Et$ at 150°. *m*-Xylene, *cyclo*propane, and $FeCl_3$ give 19% of 1 : 3 : 4-$C_6H_3Me_2Pr^{\alpha}$. C_6H_6, $Bu^{\gamma}Cl$, and $FeCl_3$ give 80% of $PhBu^{\gamma}$. With $AlCl_3$ in decahydronaphthalene at 60°, 1 : 3 : 4-$C_6H_3Me_2Bu^{\gamma}$ or -$C_6H_3Me_2{\cdot}CHMeEt$, but not -$C_6H_3Me_2Bu^{\alpha}$ or -$C_6H_3Me_2Bu^{\beta}$, gives $CHMe_3$. 1 : 3 : 4-$C_6H_3Me_2Et$ and $AlCl_3$ at 130° give a little 1 : 3 : 5-$C_6H_3Me_2Et$. The following derivatives are used for identification: *di-acetamido-*1 : 3-*dimethyl-*4-n-, m.p. 240°, -4-iso-, m.p. 255°, -4-sec.-, m.p. 266°, -4-tert.-, m.p. 294°, -5-sec.-, m.p. 278°, and -5-tert.-, m.p. 310°, *-butylbenzene*. *Dibenzamido-*1 : 3-*dimethyl-*4-n-, m.p. 225°, -4-iso-, m.p. 210°, -4-sec.-, m.p. 195°, -4-tert.-, m.p. 310°, -5-sec.-, m.p. 255°, and -5-tert.-, m.p. 285°, *-butylbenzene*. R. S. C.

Alkylation of diphenyl using alkyl sulphates in Friedel–Crafts syntheses. J. Epelberg and A. Lowy (*J. Amer. Chem. Soc.*, 1941, **63**, 101—103).—Ph_2, $AlCl_3$, and Et_2SO_4 (best 1 : 1·25 : 1·5 mol.) at 5—8° (later, 24°) or Ph_2, $AlCl_3$, and Me_2SO_4 (best 1 : 1·44 : 2·5 mol.) at 42° in *o*-$C_6H_4Cl_2$ give mainly *m*- with some *p*-C_6H_3PhAlk and mixed $C_6H_3PhAlk_2$ including the 1 : 4 : 4′-, 1 : 3 : 4′-, and 1 : 2 : 3′-compounds. Structures are elucidated by oxidation. R. S. C.

Polymethyl aromatic hydrocarbons. II. Dehydration and cyclisation of ε-phenyl-β-methyl-*n*-hexane-βε-diol. M. C. Kloetzel (*J. Amer. Chem. Soc.*, 1940, **62**, 3405—3410; cf. A., 1940, II, 302).—$COPh{\cdot}[CH_2]_2{\cdot}CO_2Me$ (**I**) and MgMeI in boiling Et_2O give 88% of *β-phenyl-ε-methyl-*n*-hexane-βε-diol* (**II**), m.p. 74—75°. Distillation of (**II**) in vac. gives approx. equal amounts of *2-phenyl-2 : 5 : 5-trimethyltetrahydrofuran* (**III**), b.p. 233·8—234·2°/769 mm., 65°/0·15 mm., and *ε-phenyl-β-methyl-*Δ^{δ}*-n-hexen-β-ol* (**IV**), b.p. 104·5—105°/0·4 mm. (*phenylurethane*, m.p. 103—104°). Distillation at 1 atm. gives almost entirely (**III**). (**IV**) decolorises Br and $KMnO_4$, with O_3 in EtOAc gives an ozonide, converted by H_2–Pd–$CaCO_3$ into COPhMe and $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CO_2H$ (*phenylurethane*, m.p. 129—130°), and is also obtained from $CPhMe{:}CH{\cdot}CH_2{\cdot}CO_2Me$, b.p. 106°/0·1 mm., by MgMeI in Et_2O. Dehydration of (**II**) by boiling, anhyd. HCO_2H gives 77% and HCl in C_6H_6 gives 93% of (**III**), HCO_2H giving also some high-boiling material. 85% H_3PO_4 converts (**II**) into a mixture (*A*), b.p. 70—76°/0·2 mm., of 1 : 1 : 4- (**V**) and, by rearrangement, 1 : 2 : 4-trimethyl-1 : 2-dihydronaphthalene (**VI**). Anhyd. HF at 25° or conc. H_2SO_4 at 0° converts (**II**) into 1 : 1 : 4-*trimethyl-*1 : 2 : 3 : 4-*tetrahydronaphthalene* (**VII**), b.p. 69°/0·2 mm., and 1 : 2 : 4-$C_{10}H_5Me_3$ (**VIII**), m.p. 54—55° [styphnate, m.p. 123—124°; picrate, m.p. 147·5—148°; *s*-$C_6H_3(NO_2)_3$ compound, m.p. 165·5—166·5°], reaction probably occurring by way of (**V**) and (**VI**) for the following reasons: (*A*) is converted by HF into (**VII**) and (**VIII**), by H_2–PtO_2 into a mixture, b.p. 66—67°/0·3 mm., of H_4-compounds, which with S at 240° gives (**VIII**), and is shown by sulphonation (see below) to contain (**VII**). (**VII**) is identified by conversion by conc. H_2SO_4 at 60—70° (stirring) into 1 : 1 : 4-trimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-*x*-sulphonic acid [NH_2Ph, m.p. 168—170° (decomp.), p-$C_6H_4Me{\cdot}NH_2$, m.p. 195—196° (decomp.),

and p-NO_2·C_6H_4·NH_2 salt, m.p. 240—241° (decomp.)], by dehydrogenation by Se at 270° (N_2) or S at 240° to 1 : 4-$C_{10}H_6Me_2$, and by oxidation ($KMnO_4$) to *o*-homophthalic anhydride (21%). CHPhMe·$[CH_2]_2$·CO_2Me, b.p. 143—144°/25 mm., and MgMeI give ε-phenyl-β-methyl-*n*-hexan-β-*ol*, b.p. 106°/0·4 mm., cyclised to (**VII**) by conc. H_2SO_4 at 0°. (OH·CPh_2·$CH_2)_2$, m.p. 204° (cf. lit.), is obtained (54%) from (**I**) by MgPhBr in Et_2O. β-1 : 2 : 3 : 4-Tetrahydro-6-naphthoylpropionic acid is obtained (77%) from tetrahydronaphthalene by $(CH_2·CO)_2O$ and $AlCl_3$ in $PhNO_2$ at 0°—room temp. Its *Me* ester, m.p. 31—32°, b.p. 165—166°/0·2 mm. (*semicarbazone*, m.p. 144°; *p-nitrophenylhydrazone*, m.p. 123—124°), and MgMeI give β-1 : 2 : 3 : 4-*tetrahydro*-6-*naphthyl*-ε-*methyl*-n-*hexane*-βε-*diol*, m.p. 89—90°, which, when distilled in vac., gives 2-1′ : 2′ : 3′ : 4′-*tetrahydro*-6′-*naphthyl*-2 : 5 : 5-*trimethyltetrahydrofuran*, b.p. 128—129°/0·2 mm., and ε-1 : 2 : 3 : 4-*tetrahydro*-6-*naphthyl*-β-*methyl*-Δ^{δ}-n-*hexen*-β-*ol*, b.p. 152—153°/0·2 mm. R. S. C.

Synthesis of 4 : 5-methylenephenanthrene. W. E. Bachmann and J. C. Sheehan (*J. Amer. Chem. Soc.*, 1941, **63**, 204—206).—7-*Bromoacenaphthene* (prep. from acenaphthenol by PBr_3 in Et_2O), m.p. 70·5—71·5°, and $CHNa(CO_2Et)_2$ in C_6H_6–EtOH at 0° (3 days) and then the b.p. (2 hr.) give an ester, hydrolysed by 40% KOH at 100° to 7-*acenaphthylmalonic acid* (82%), m.p. 174—175°, which at 190° gives 7-*acenaphthylacetic acid*, m.p. 116—117°, sublimes at 160°/0·5 mm. With, successively, $SOCl_2$–Et_3O and a trace of C_5H_5N, CH_2N_2, and Ag_2O–MeOH, this gives 78% of β-7-*acenaphthylpropionic acid*, m.p. 108·5—109·5°, sublimes at 160°/0·5 mm. The chloride derived therefrom by PCl_5–C_6H_6 is cyclised by $SnCl_4$ in C_6H_6 to 1-*keto*-4 : 5-*methylene*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (92%), m.p. 124·5—125·5°, sublimes at 150°/0·01 mm., which with $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ gives 1-*hydroxy*-4 : 5-*methylene*- (**I**) (87%), m.p. 113—114°, and with Zn–Hg–HCl–AcOH–PhMe gives 4 : 5-*methylene*- (**II**) (63%), m.p. 55·5—56·5°, sublimes at 160°/0·5 mm., -1 : 2 : 3 : 4-*tetrahydrophenanthrene*. Pd–C at 280—300° converts (**I**) or crude (**II**) in N_2 into 4 : 5-methylenephenanthrene, m.p. 114·3—115·3° (picrate, m.p. 165·8—166·5°), in 86 and 52% yield, respectively. R. S. C.

Scianthrene. Synthesis of 7-methyl-1-*iso*propylphenanthrene. (Miss) R. M. Orcutt and M. T. Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 127—131).—7-*Methyl*-1-iso*propylphenanthrene* (**I**) is synthesised and found to differ from scianthrene (Uota, A., 1937, II, 158). 2 : 6-$C_{10}H_6Me$·CO·$[CH_2]_2$·CO_2Me and $MgPr^{\beta}I$ in Et_2O–C_6H_6 at ~70° give an intractable acid, converted by esterification and distillation into *Me* γ-6-*methyl*-2-*naphthyl*-δ-*methylhydrosorbate*, b.p. 185°/2 mm. The crude acid derived therefrom with 2% Na–Hg and NaOH in boiling abs. EtOH gives an acid, converted by esterification into *Me* γ-6-*methyl*-2-*naphthyl*-δ-*methyl*-n-*hexoate*, b.p. 175°/2 mm., whence hydrolysis and subsequent treatment with PCl_5 in boiling C_6H_6 gives the acid chloride. Ring-closure by $AlCl_3$ in C_6H_6 at, successively, 0°, room temp., and the b.p. gives 74% of 4-*keto*-7-*methyl*-1-iso*propyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 75—76°, b.p. 175°/2 mm. [*oxime*, m.p. 205° (decomp. from ~200°)], reduced by Zn–Hg–PhMe–HCl to 7-*methyl*-1-iso*propyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (55%), b.p. 175°/2 mm. Se at 320—340° then yields (**I**), m.p. 82—83° [*picrate*, m.p. 119—120°; *styphnate*, m.p. 148—149°; $C_6H_2(NO_2)_3$·CO_2H additive *compound*, m.p. 163—164°; derived *quinone*, m.p. 188—190° (darkens at ~180°), and *quinoxaline*, m.p. 119—120°]. γ-*Keto*-γ-6-*methyl*-1-*naphthylbutyric acid* [isolated in ~38% yield as by-product of the condensation of 2-$C_{10}H_7Me$ with $(CH_2·CO)_2O$], m.p. 141—143°, and Zn–Hg–PhMe–HCl give γ-6-*methyl*-1-*naphthylbutyric acid*, m.p. 116—118° (*Me* ester, b.p. 160°/2 mm.), cyclised (as above) to 1-*keto*-7-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 92—94° [*semicarbazone*, m.p. 258° (sinters and decomp. ~244°)]. Condensation with $MgPr^{\beta}I$ in Et_2O–C_6H_6 and subsequent dehydration by $KHSO_4$ gives 7-*methyl*-1-iso*propyl*-1 : 2-*dihydrophenanthrene* (38%), b.p. 150°/2 mm., dehydrogenated to (**I**) by Se at 290—320°. Identity of the products of the two syntheses proves the structure. M.p. are corr. R. S. C.

Polyeyclic aromatic hydrocarbons. XXVII. G. M. Badger, F. Goulden, and F. L. Warren (*J.C.S.*, 1941, 18—20).—1 : 2-Dimethylanthraquinone with MgMeI yields 1 : 2 : 9 : 10-*tetramethyl*-9 : 10-*dihydroanthracene* (?), m.p. 100—101°, which could not be satisfactorily dehydrogenated. Anthracene with Na in Et_2O followed by MeI at 0° yields 9 : 10-*dimethyl*-9 : 10-*dihydro*-, m.p. 101—102°, dehydrogenated (S at 230°) to 9 : 10-dimethyl-anthracene, also obtained by reducing 9 : 10-dimethyl-9 : 10-dihydroanthraquinol with red P and HI in AcOH. Dehydration of 9 : 10-dimethyl-9 : 10-dihydro-1 : 2-benzanthraquinol (conc. H_2SO_4 in C_6H_6–MeOH) and -1 : 2 : 5 : 6-dibenzanthraquinol (picric acid, followed by boiling EtOH) yields the 9 : 10-*oxides*, m.p. 120—121° and 140—141° (*picrate*, m.p. 107—108°) respectively, reduced (HI in AcOH and MgMeI respectively) to 9 : 10-dimethyl-1 : 2-benz- and -1 : 2 : 5 : 6-dibenz-anthracene. A. Lt.

Structure of the "7-dehydrocholestene isomeride." J. C. Eck and E. W. Hollingsworth (*J. Amer. Chem. Soc.*, 1941, **63**, 107—111).—The product (**I**), m.p. 84—85°, previously (Eck *et al.*, A., 1939, II, 105) considered to be $\Delta^{4:6}$-cholestadiene (**II**), is an inseparable mixture of the true (**II**) ("7-dehydrocholestene isomeride," m.p. 90—91°) and coprostene. HCl in $CHCl_3$ converts (**II**) at 0° or Δ^5-cholesten-7-ol (**III**) at room temp. into $\Delta^{3:5}$-cholestadiene. Br and (**I**) in AcOH containing a little $COMe_2$ at 0° give coprostene dibromide. Dehydration of (**III**) by Al_2O_3 gives ? (**II**) or other products according to the temp. $\Delta^{4:6}$-Cholestadien-3-onesemicarbazone and NaOEt–EtOH at 200° give a mixture containing (**II**), whence *cholestenedione* (**IV**) is obtained by CrO_3. (**I**) is also obtained from α-5 : 6-dibromocholestane by $AgNO_3$ in C_5H_5N at room temp. (1 month). CrO_3 oxidises (**I**) to (**IV**), m.p. 160—161°, $[\alpha]_D^{32}$ −51·7° in CCl_4, the *disemicarbazone*, m.p. 322° (decomp.), of which with NaOEt–N_2H_4–EtOH at 200° gives coprostene. R. S. C.

Carcinogenic hydrocarbons. IV. Bromination of hydrindene. Briefer synthesis of cholanthrene. W. F. Bruce (*J. Amer. Chem. Soc.*, 1941, **63**, 301—303; cf. A., 1939, II, 105).—Hydrindene and Br, best in AcOH, give a 1 : 2 mixture of α- and β-Br-compounds, the proportions being established by oxidation to *x* : 1 : 2-$C_6H_3Br(CO_2H)_2$ and esterification of the unhindered acid. The mixture is converted into α-naphthoylhydrindenes and thence into cholanthrene in 8% over-all yield. R. S. C.

Cyclic methyleneimines. III. Hydrolysis of quaternary compounds. Preparation of secondary amines. J. Graymore (*J.C.S.*, 1941, 39—41; cf. A., 1940, II, 27).—*NN′N″*-Trimethyltrimethylenetriamine [Cl_2 in $CHCl_3$ gives the *dichloride*, m.p. 128—130° (decomp.)] and CH_2PhCl (in ice–salt) for 1 day afford a mixture, $C_6H_{15}N_3$ + 1 and 2 CH_2PhCl, m.p. 115—117°, hydrolysed (aq. HCl) to CH_2O, CH_2Ph·NHMe, CH_2Ph·NMe_2, and NH_2Me. Some *dibenzyldimethylammonium chloride*, m.p. 85—90° (indistinct) (purified through its *mercurichloride*, m.p. 167—168°), is also formed. *NN′N″*-Triethyltrimethylenetriamine (**I**) and CH_2PhCl give a mixture hydrolysed (HCl) to NH_2Et, CH_2Ph·NHEt (*picrate*, m.p. 122—123°), and CH_2Ph·NMeEt. (**I**) and CH_2:CH·CH_2I in Et_2O readily afford an additive product, hydrolysed to NH_2Et, and ethylallylamine (*picrate*, m.p. 102°). (**I**) and EtBr–Et_2O (slowly) give a quaternary *compound*, $C_{11}H_{26}N_3Br$, m.p. 112—114° (decomp.) (10% yield), hydrolysed to NH_2Et and $NHEt_2$. A. T. P.

Freedom of rotation about the carbon–carbon ethylenic linking. Substituted stilbenes. M. Calvin and R. E. Buckles (*J. Amer. Chem. Soc.*, 1940, **62**, 3324—3328).—*trans*-(*p*-NO_2·C_6H_4·CH:)$_2$ or the *cis*-isomeride obtained therefrom by irradiation (Hg lamp) in $PhNO_2$ at 80—90° is reduced by aq. Na_2S–H_2S in boiling 95% EtOH to 4-*nitro*-4′-*aminostilbene* (**I**) (60%), m.p. 245—245·5°, and 4-*nitro*-4′-*ethylaminostilbene*, m.p. 222·5—223°; complete reduction (best with Sn and EtOH–conc. HCl) gives only *trans*-(*p*-NH_2·C_6H_4·CH:)$_2$. In 0·25—0·5N-HCl, (**I**) gives a red and in 1—2N-HCl (or 0·25N-HCl + 3·5N-NaCl) gives a yellow *hydrochloride*, both melting at 245° after decomp. from ~230°, probably the cis- and trans-*forms*, respectively. Both salts regenerate (**I**) in H_2O, alkali, or 0·1N-HCl. In abs. EtOH, (**I**) has an intense absorption max. at 4095 and a weaker max. at 2890 A. In 4·8 × 10^{-4} and 3N-HCl–EtOH, (**I**) has absorption max. at 3310 and 3470 A., respectively, the difference corresponding with the existence of two hydrochlorides; in acid of intermediate concn. intermediate absorption is recorded. The absorption in acid resembles those of *trans*- (**II**) (prep. from *p*-NO_2·C_6H_4·CH_2·CO_2H, PhCHO, and piperidine at 150—160°) and *cis*-*p*-NO_2·C_6H_4·CH:CHPh [prep. from (**II**) by illumination and converted into (**II**) at 170°]. The ready interconversion of *cis*- and *trans*-forms of (**I**) occurs by equilibration of the base and ion. Equilibration of the two forms of the salt

probably occurs by way of a diradical; effects of resonance are discussed. R. S. C.

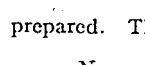
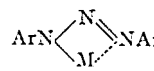
Hydrogenation of arylnaphthylamines.—See B., 1941, II, 74.

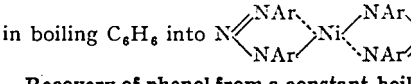
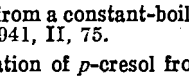
Thioanilides of malonic acids. A. A. Morton, A. R. Olson, and J. W. Blattenberger (*J. Amer. Chem. Soc.*, 1941, **63**, 314—315).—*n*-$C_6H_{11}Na$ (**I**) or CH_2PhNa [from (**I**) and boiling PhMe] and PhNCS in light petroleum (not in a creased flask; A., 1939, I, 283) give 2% of *butyl-*, m.p. 67—68°, or 2·4% of *phenyl-malondi(thioanilide)*, m.p. 66—67°, respectively. (**I**) with CS_2, SO_2, or SO_3 gives mixtures. R. S. C.

Arylsulphonylcarbamides. E. H. Cox and S. M. Raymond, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 300—301).—$NH{:}C(OEt)\cdot NH_2$ (prep. in 80% yield from $CN\cdot NH_2$ and $CN\cdot NH_2$,2HCl in abs. EtOH at 55—65°) and $ArSO_2Cl$ in aq. NaOH at 0° give *benzene-*, m.p. 101°, p-*toluene-*, m.p. 79°, and 1-*naphthalene-sulphonylethylisocarbamide*, $ArSO_2\cdot N{:}C(OEt)\cdot NH_2$, m.p. 145°, converted by conc. HCl into benzene-, m.p. 169°, p-*toluene-*, m.p. 192°, and 1-*naphthalene-sulphonylcarbamide*, m.p. 211°, respectively. R. S. C.

Separation and determination of *p*-phenylenediamine in mixtures.—See B., 1941, II, 70.

Reactivity of the methyl group. VII. Derivatives of azobenzene. L. Chardonnens and P. Heinrich (*Helv. Chim. Acta*, 1940, **23**, 1399—1418; cf. A., 1940, II, 160).—Me in C_6H_4 is rendered active by the simultaneous presence of NO_2 and PhN_2 in the *o-* and *p*-position respectively. Less defined results are obtained when the substituents are in the reversed positions. 3 : 4 : 1-$NO_2\cdot C_6H_3Me\cdot N{:}NPh$ (**I**) is slowly converted by PhCHO in presence of a considerable proportion of piperidine at 165—175° into 3-*nitro*-4-*styrylazobenzene*, m.p. 136—137° (*dibromide*, m.p. 166·5°), in 76% yield. Similarly *p*-$NMe_2\cdot C_6H_4\cdot CHO$ affords 3-*nitro*-4-p-*dimethylaminostyrylazobenzene*, m.p. 170·5°, which gives a carmine-red solution in conc. H_2SO_4. 3 : 3′-Dinitro-4 : 4′-dimethylazobenzene and PhCHO react briskly at 175—185° giving 3 : 3′-*dinitro*-4 : 4′-*distyrylazobenzene*, m.p. 260—261° [*tetrabromide*, m.p. 234—235° (decomp.)]. 3 : 3′-*Dinitro*-4 : 4′-*di*-p-*dimethylaminostyrylazobenzene* has m.p. >320°. After prolonged boiling in EtOH containing calcined Na_2CO_3, (**I**) and *p*-$NO\cdot C_6H_4\cdot NMe_2$ give much unchanged material, 3-*nitroazobenzene*-4-*carboxy*-p-*dimethylaminoanilide* (**II**), m.p. 209°, and 2-*nitro*-4-*benzeneazobenzaldehyde*-p-*dimethylaminoanil*, m.p. 164—165°. With *p*-$NO\cdot C_6H_4\cdot NEt_2$ and PhNO respectively, (**I**) gives unchanged material and 2-*nitro*-4-*benzeneazobenzaldehyde*-p-*diethylaminoanil*, m.p. 156·5°, and 3-*nitroazobenzene*-4-*carboxyanilide* (**III**), m.p. 174·5°. The above anils are hydrolysed by 10% HCl in presence of C_6H_6 to 2-*nitro*-4-*benzeneazobenzaldehyde* (**IV**), m.p. 97° [*oxime*, m.p. 142—143°; *phenylhydrazone*, m.p. 195—196° (decomp.); *semicarbazone*, m.p. 256° (decomp.)]. This is oxidised (CrO_3 in 90% AcOH) to 3-*nitroazobenzene*-4-*carboxylic acid*, m.p. 191° after softening [*Me* ester, m.p. 110°; *anilide*, m.p. 174·5°, identical with (**III**); p-*dimethylaminoanilide*, m.p. 209°, identical with (**II**)]. NaOH transforms (**IV**) in $COMe_2$ into 6 : 6′-*dibenzeneazoindigotin*, m.p. >300°. 2 : 1 : 4-$NH_2\cdot C_6H_3Me\cdot NO_2$ is transformed by $K_2S_2O_8$ in dil. H_2SO_4 at <10° into 2-*nitroso*-4-*nitrotoluene*, m.p. ~165—170° (decomp.) after becoming green at 131°, which is slowly converted by NH_2Ph in AcOH at 60° into 5-*nitro*-2-*methylazobenzene* (**V**), m.p. 92°, also obtained similarly from PhNO and 2 : 1 : 4-$NH_2\cdot C_6H_3Me\cdot NO_2$; (**V**) does not appear to react with aldehydes. 5 : 5′-Dinitro-2 : 2′-dimethylazobenzene, m.p. 273°, PhCHO, and piperidine at 175—185° give 5 : 5′-*dinitro*-2 : 2′-*distyrylazobenzene*, m.p. 265° (decomp.). (**V**) is converted by prolonged treatment with *p*-$NO\cdot C_6H_4\cdot NMe_2$, *p*-$NO\cdot C_6H_4\cdot NEt_2$, or PhNO in boiling EtOH containing anhyd. Na_2CO_3 into 6-*nitro*-2-*phenylindazole*, m.p. 149°, the constitution of which is established by its formation by the reduction ($SnCl_2$) of 2 : 4-dinitrobenzylaniline and by its oxidation (CrO_3 in AcOH) to 5-*nitroazobenzene*-2-*carboxylic acid*, m.p. ~164—166° (*Me* ester, m.p. 108·5°). PhNO and 2 : 1 : 6-$NH_2\cdot C_6H_3Me\cdot NO_2$ in glacial AcOH afford 3-*nitro*-2-*methylazobenzene*, m.p. 86°, transformed by *p*-$NO\cdot C_6H_4\cdot NMe_2$ in boiling EtOH containing Na_2CO_3 into 4-nitro-2-phenylindazole, m.p. 157°, in very small yield. H. W.

Chelation in metallic triazen salts. F. P. Dwyer (*J. Amer. Chem. Soc.*, 1941, **63**, 78—81).—Absence of isomerism among *N*-Me derivatives of the NHPh·N:NPh (**I**) series is due to chelation of the metallic salts from which they are prepared. These salts show resonance,   . Na_2PdCl_4, (**I**), and NaOAc in aq. MeOH give *trisdiazoaminobenzenepalladium* (**II**), brown, m.p. 120—125° (decomp.), which in C_5H_5N at 0° gives *bispyridine-*, orange, and with $(CH_2\cdot NH_2)_2$ (**III**) in warm C_6H_6 gives *ethylenediamine-bisdiazoaminobenzenepalladium*, yellowish-brown; in this series the Pd is hexacovalent. When kept in solution overnight or warmed in $COMe_2$ at 50°, (**III**) gives *bisdiazoaminobenzenepalladium* (as annexed), red-dish-brown, decomp. >300° (incandescence). *Tris-* and *bis*-4 : 4′-*dimethyldiazoaminobenzenepalladium*, decomp. >300°, are similarly prepared. The tetracovalent Pd compounds are monomeric at low concn., but there is a slight tendency to association at higher concn. (ebullioscopy in C_6H_6), a tendency shown also by the triazens themselves (cryoscopy in C_6H_6). $Cu(OAc)_2$ and (**I**) in MeOH at 0° give pure bisdiazoaminobenzene-copper^{II}, green, decomp. 120—130°, which in hot C_5H_5N (not with C_6H_5N in cold C_6H_6) gives *bispyridine-* (**IV**), indigo-blue, and with (**III**) at 40° (not in cold C_6H_6) gives *ethylenediamine-bisdiazoaminobenzenecopper*^{II}, $+C_6H_6$ (lost at 90—100°), m.p. 140—143° (gas evolved at 145°). *Bis*-4 : 4′- and *bispyridinebis*-4 : 4′-*dimethyldiazoaminobenzenecopper*^{II} are similarly prepared. When NaOH is added to CuCl, (**I**), and C_5H_5N in EtOH in absence of air, *bispyridinediazoaminobenzenecopper*^{I} is obtained. At 100° this gives *diazoaminobenzenecopper*^{I}, dimorphic, m.p. 280°, obtained also by heating the Cu^{II} compounds. $AgOAc,2C_5H_5N$ in MeOH gives *diazoaminobenzene-* and 4 : 4′-*dimethyldiazoaminobenzene-silver*, which do not add bases. R. S. C.

Diamagnetism of nickel triazen complexes. F. P. Dwyer and D. P. Mellor (*J. Amer. Chem. Soc.*, 1941, **63**, 81—83).—$Ni(OAc)_2$, C_5H_5N, NHPh·N:NPh, and NaOH in aq. MeOH at 80° give *bispyridinebisdiazoaminobenzenenickel* (**I**), converted at 120—130° into *bisdiazoaminobenzenenickel* (**II**), m.p. 278°, explodes at 285°, which adds C_5H_5N at 100° and $(CH_2\cdot NH_2)_2$ in boiling C_6H_6 to give (**I**) and the *ethylenediamine* derivative, m.p. 148°, respectively. *Bispyridinebis*-4 : 4′- and *bis*-4 : 4′-*dimethyldiazoaminobenzenenickel* (**III**), explodes at 200°, are similarly prepared. (**II**) and (**III**) are diamagnetic and thus contain square co-ordinated, and therefore chelated, Ni. Mol. wts. indicate structures  , dissociating partly in boiling C_6H_6 into  . R. S. C.

Recovery of phenol from a constant-boiling mixture of phenol and water.—See B., 1941, II, 75.

Isolation and separation of *p*-cresol from tar acid mixtures.—See B., 1941, II, 75.

Velocity of reduction of phenols. I. Monohydric phenols. V. I. Bobischev, M. K. Djakova, and A. V. Lozovoi (*J. Appl. Chem. Russ.*, 1940, **13**, 942—950).—The relative velocities of reduction of phenols (PhOH = 100) by H_2 at 350°/31 atm. (MoS_2 catalyst) are: *o-* 60·8, *m-* 108, and *p*-cresol 126, 1 : 2 : 4-65·2, 1 : 3 : 5- 65·5, and 1 : 3 : 4-$C_6H_3Me_2\cdot OH$ 70·2, thymol 65·8, carvacrol 44·9, *α-* 160, and *β*-$C_{10}H_7\cdot OH$ 208, PhSH 2845. The products of hydrogenation are: aromatic hydrocarbons 87—98, naphthenes 0·6—9·6, naphthylenes 0—4·1%. The velocity of reduction of OH, and of hydrogenation of the C_6H_6 ring, rises with increasing H_2 pressure. R. T.

Bromination of phenols by means of bromide–bromate solution. M. M. Sprung (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 35—38).—PhOH and *m*-$C_6H_4R\cdot OH$ react with acid KBr–$KBrO_3$ giving quant. substitution in the *o-* and *p*-positions. Some phenols with *sec.-* or *tert.*-alkyl groups in *o-* or *p*-position also brominate quantitatively. Phenols with *o-* or *p*-primary alkyl groups give results 10—150% too high depending on the alkyl groups. Certain phenols with *p*-primary alkyl groups can be determined accurately by bromination at low temp., but the conditions must be worked out for each phenol. J. D. R.

Products of condensation of phenol with benzaldehyde. I. I. P. Losev and M. S. Akutin. **II.** I. P. Losev and V. N. Kotrelev (*J. Appl. Chem. Russ.*, 1940, **13**, 916—925, 926—933).—I. 1 : 2 PhCHO–PhOH mixtures are heated for 2 hr. at 160° with 2% of HCl. The resinous product is dissolved in C_6H_6, and fractionally pptd. with light petroleum. The numerous fractions when further fractionated yield finally the following amorphous or cryst. products: $(p\text{-OH·C}_6\text{H}_4)_2\text{CHPh}$, $\text{COPh·C}_6\text{H}_4\text{·OH-}p$, $\text{OH·CHPh·C}_6\text{H}_4\text{·OH-}p$, and benzaurin (**I**). The resin thus appears to consist of products of condensation of 1 and 2 mols. of PhOH with 1 mol. of PhCHO.

II. The resin is extracted exhaustively with aq. NH_3 at room temp., and the extract neutralised with HCl and extracted with $CHCl_3$. The residue from the $CHCl_3$ when recrystallised from C_6H_6 yields (**I**), m.p. 156—157° (yield 3%). The extracted resin is dissolved in C_6H_6 and fractionally pptd. as above. In addition to the substances previously identified the following were found: 2 : 6- and 2 : 7-dihydroxy-9 : 10-diphenylanthracene and 2 : 4 : 1-$C_6H_3Bz_2$·OH. Other cryst. products were isolated, but not identified. R. T.

Determination of molecular symmetry in the αβ-diethyldibenzyl [γδ-diphenylhexane] series.—See A., 1941, I, 103.

Syntheses in the naphthalene and anthracene series. J. B. Niederl and R. H. Nagel (*J. Amer. Chem. Soc.*, 1941, **63**, 307—308).—$(CH_2Ac)_2$ and 1 : 2 : 3-$C_6H_3(OH)_3$ in 70% H_2SO_4 at 0° give 1 : 2 : 3-*trihydroxy*-5 : 8-*dimethylnaphthalene*, m.p. 187° [*triacetate*, m.p. 148—150°; *triphenylurethane*, m.p. 198°]. $(CH_2Ac)_2$ and quinol in H_2SO_4–AcOH–H_2O give 1 : 4 : 5 : 8-*tetramethylanthraquinone*, m.p. 235°. R. S. C.

Preparation of phenyl diphenylyl ethers.—See B., 1941, II, 75.

1- and 2-Methoxytriphenylene. W. S. Rapson (*J.C.S.*, 1941, 15—18).—A convenient synthesis of triphenylene derivatives is described. 2-*cyclo*Hexenyl*cyclo*hexanone (**I**) (modified prep.) and MgPhBr afford 2-*cyclo*hexenyl-1-phenyl*cyclo*hexanol (**II**), b.p. 170—175°/3 mm., which with Se at 320—340° gives a small yield of triphenylene (**III**). (**II**) and H_2SO_4–AcOH at room temp. for 5 min. give an oil, probably 2-cyclo*hexenyl*-1-*phenyl*cyclo*hexene*, b.p. 155—160°/4 mm., converted by Se into (**III**) (low yield). (**II**) and $AlCl_3$ (or $SnCl_4$)–CS_2 at 0° to room temp. (5 hr.) afford a mixture, b.p. 180—250°/4 mm., which affords the picrate, m.p. 185°, of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrotriphenylene*, m.p. 129—130°, converted by Pd–C at 300° into an almost quant. yield of (**III**). The filtrate from the picrate gives only an impure oil, b.p. 175—185°/4 mm., which with Se gives some (**III**). *p*-OMe·C_6H_4·MgBr and 2-*cyclo*hexyl*cyclo*hexanone yield an oil, b.p. 205—210°/5 mm. (some dehydration), which with Se at 300—320° does not give cryst. material.

[With E. Rollnick.] (**I**) and *p*-C_6H_4Me·MgBr similarly lead to 2-*methyl*-5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-*octahydrotriphenylene*, m.p. 93—94° [picrate, m.p. 195·5° (slight previous sintering)], and thence (Pd–C) 2-methyltriphenylene. (**I**) and *o*-OMe·C_6H_4·MgBr give an oil, b.p. 188—192°/6 mm. (Se affords no definite compound), which with $AlCl_3$ (not $SnCl_4$) in CS_2 affords 1-*methoxy*-5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-*octahydrotriphenylene*, m.p. 96—97° (purified through the picrate, m.p. 204—205°), and thence by Pd–C at 300° 1-*methoxytriphenylene*, m.p. 172° (picrate, m.p. 196—198°), unchanged on boiling with HI (*d* 1·7) for 10 hr. (**I**) and *p*-OMe·C_6H_4·MgBr yield 2-*cyclo*hexenyl-1-*p*-anisyl*cyclo*hexanol (**IV**), b.p. 193—197°/7 mm., which with Se at 340° for 12 hr. affords a trace of 2-*hydroxytriphenylene* (**V**), m.p. 213—215° (previous sintering) (*acetate*, m.p. 129°). (**IV**) and $AlCl_3$–CS_2 afford 2-*methoxy*-5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-*octahydrotriphenylene*, m.p. 120—121° (picrate, m.p. 193—194°), converted (Pd–C) into 2-*methoxytriphenylene*, m.p. 97—98°, and thence by HI (*d* 1·7)–AcOH into (**V**). 2-*cyclo*Hexyl-1-phenyl*cyclo*hexanol and Se afford a little (**III**) (cf. Nenitzescu *et al.*, A., 1937, II, 140); 2-*cyclo*hexyl-1-*p*- or -*o*-anisyl*cyclo*hexanol similarly gives no definite product. A. T. P.

Reaction of aminophenols with copper and iron. (A) L. M. Kulberg. (B) V. A. Nazarenko (*J. Appl. Chem. Russ.*, 1940, **13**, 630—632, 633—637).—(A) Polemical, against Nazarenko (A., 1939, II, 313).

(B) A reply. R. T.

Condensation of phenols with amines and formaldehyde. H. A. Bruson and C. W. MacMullen (*J. Amer. Chem. Soc.*, 1941, **63**, 270—272).—Addition of 30% CH_2O (3·5 mols.) to PhOH (1 mol.) and 25% $NHMe_2$ (4 mols.) at >30° and heating at 90—95° gives 2 : 4 : 6-*tri*(*dimethylaminomethyl*)*phenol* (86%), b.p. 130—135°/1 mm., converted by Ac_2O at 90—95° into 2 : 4 : 6-*tri*(*acetoxymethyl*)*phenyl acetate*, b.p. 200—205°/1 mm., the structure of which is proved by hydrogenation (Raney Ni; 150°/1500 lb.) to mesitol. 2 : 4 : 6-*Tri*(*morpholinomethyl*)*phenol*, m.p. 106—107°, is similarly obtained. *m*-Cresol, $NHMe_2$, and CH_2O give an oil, b.p. 200°/0·5 mm., converted by boiling Ac_2O into 2 : 4 : 6-*tri*(*acetoxymethyl*)-*m*-*tolyl acetate*, b.p. 194—204°/1 mm. R. S. C.

Physostigmine substitutes. J. R. Stevens and R. H. Beutel (*J. Amer. Chem. Soc.*, 1941, **63**, 308—311).—The following are prepared, usually by reactions of the type, PhOH → NPh·N·C_6H_4·OH (+H_2–catalyst) → NH_2·C_6H_4·OH → NR_2·C_6H_4·OH (+ NMe_2·COCl–C_5H_5N) → NR_2·C_6H_4·O·CO·NMe_2 (*A*), and NR_2·C_6H_4·OH + MeCNO → NR_2·C_6H_4·O·CO·NHMe (*B*); (*A*) and (*B*) are then converted into methiodides. p-*Dimethylaminophenyl dimethylurethane methiodide*, m.p. 195·5—196°. 5-Dimethylamino-*o*- (*hydrochloride*, m.p. 189°; *methiodide*, m.p. 189—190°) and 6-dimethylamino-*m*-tolyl (*hydrochloride*; *methiodide*, m.p. 169°), 4-dimethylamino-3-ethyl- (*hydrochloride*, m.p. 144—144·5°; *methiodide*, m.p. 149·5°) and -3-*iso*propyl-phenyl (*methiodide*, m.p. 170°), 6-dimethylaminothymyl (*hydrochloride*, m.p. 162—164°; *methiodide*, m.p. 171·5°), 5-dimethylaminocarvacryl (*hydrochloride*, m.p. 185·5°; *methiodide*, m.p. 169·5°), 3-dimethylamino-*p*-tolyl (*hydrochloride*, m.p. 174·5°; *methiodide*, m.p. 154—155°), 2-dimethylamino-4-ethyl- (*hydrochloride*, m.p. 144—145°; *methiodide*, m.p. 148—149°), -4-*iso*propyl- (*hydrochloride*, m.p. 168·5°; *methiodide*, m.p. 171°), -4-*tert.*-butyl- (*hydrochloride*, m.p. 186·5°; *methiodide*, m.p. 162°), and -4-*tert.*-amyl-phenyl (*hydrochloride*, m.p. 175·5—176·5°; *methiodide*, m.p. 146·3°) dimethylurethane. Prostigmine, m.p. 143° (*methiodide*, m.p. 162—163°; *hydrochloride*, m.p. 89°). 6-Dimethylaminothymyl (*hydrochloride*, m.p. 199°; *methiodide*, m.p. 182°) and 5-dimethylaminocarvacryl methylurethane (*hydrochloride*, m.p. 192°; *methiodide*, m.p. 159°). Physostigmine methiodide, m.p. 188°. 3-*Hydroxypyridine hydrochloride* has m.p. 89°. The methiodides show physostigmine-like activity, though in widely varying degree. Prep. of *p*-$C_6H_4Pr^{\beta}\cdot NO_2$ from $PhPr^{\beta}$ by HNO_3 (*d* 1·44) and H_2SO_4 at 20—30°, later 40°, and thence of *p*-$C_6H_4Pr^{\beta}\cdot NH_2$ and -$C_6H_4Pr^{\beta}$·OH, m.p. 60°, is detailed. 2-*Amino*-4-*ethyl*-, m.p. 139·5°, -4-iso*propyl*-, m.p. 136°, -4-tert.-*butyl*-, m.p. 161·5°, and -4-tert.-*amyl*-*phenol*, m.p. 120°, 2-*dimethylamino*-4-*ethyl*-, m.p. 157°, -4-iso*propyl*-, m.p. 172°, and -4-tert.-*butyl*-*phenol hydrochloride*, m.p. 217—218°, 2-*dimethylamino*-4-tert.-*amylphenol*, m.p. 44—45°, 4-*amino*-3-*ethyl*-, m.p. 169·5°, and -3-iso*propyl*-*phenol*, m.p. 175·5°, 4-*dimethylamino*-3-*ethyl*-, m.p. 179—180°, and -3-iso*propyl*-*phenol hydrochloride*, m.p. 218—219°, 6-*dimethylaminothymol hydrochloride*, m.p. 203—204°, and 5-*dimethylaminocarvacrol hydrochloride*, m.p. 216—216·5°, are reported. R. S. C.

Detoxication. VIII. Alleged formation of *p*-hydroxylaminobenzenesulphonamide and *p*-aminophenol from sulphanilamide *in vivo*; colour reactions used for detection; possible formation of aminophenolsulphonamides. W. V. Thorpe and R. T. Williams [with (in part) J. Shelswell]. **IX. Synthesis of possible biological oxidation products of sulphanilamide.** W. V. Thorpe and R. T. Williams (*Biochem. J.*, 1941, **35**, 52—60, 61—65).—VIII. The colour reactions (*e.g.*, Pucher and Day; Rosenthal and Bauer; indophenol) previously used for the detection of these compounds are non-sp.; thus, NHPh·OH gives all the colour reactions of *p*-OH·NH·C_6H_4·SO_2·NH_2 and 1 : 3 : 4-NH_2·C_6H_3(OH)·SO_2·NH_2 those of *p*-aminophenol. There is no reliable evidence of the biological formation of NHAr·OH from sulphanilamide.

IX. 1-*Hydroxybenzoxazole*-5-*sulphonyl chloride*, m.p. 186—187° (from the Na salt and PCl_5), and conc. aq. NH_3 give the *amide*, m.p. 263° [*Na* salt (+ $2H_2O$)], hydrolysed by 30% NaOH to 4-*amino*-3-*hydroxybenzenesulphonamide*, m.p. 164° (*hydrochloride*, decomp. >300° without melting; ON⁴-*Bz*$_2$ derivative, m.p. 191°), which slowly causes the formation of methæmoglobin (**I**) *in vitro*. Acetylation (Ac_2O–C_5H_5N) of 4 : 2 : 1-NH_2·C_6H_3(OH)·SO_3H gives 4-acetamido-2-acetoxybenzenesulphonic acid (as C_5H_5N salt, m.p. 170—172°), the *chloride*, m.p. 169°, of which with aq. NH_3 affords 4-*acetamido*-2-*hydroxybenzenesulphonamide* (**II**), m.p. 280° (decomp.) (rapid

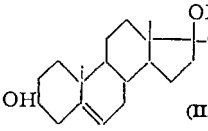
heating), and a *substance* (? mixture) (**III**), m.p. 235°. Hydrolysis (2N-NaOH or -HCl) at 100° (bath) of (**II**) or (**III**) gives *4-amino-2-hydroxybenzenesulphonamide*, m.p. 152° (hydrochloride), which does not cause formation of (**I**). 4 : 2 : 1-$NO_2{\cdot}C_6H_3(NH_2){\cdot}SO_3H$ [NH_4 salt, orange (labile), passing at ~80° into a red (stable), form] and $ClSO_3H$ gave (in one experiment only) some chloride, whence *4-nitro-2-aminobenzenesulphonamide*, m.p. 215°. P. G. M.

Action of thionyl chloride, sulphur dichloride, and sulphur monochloride on naphthol derivatives. J. W. Airan and S. V. Shah (*J. Univ. Bombay*, 1940, **9**, Part 3, 115—126).—2 : 1-$C_{10}H_6Ac{\cdot}OH$ (**I**) with $SOCl_2$ or SCl_2 in C_6H_6 in presence of $ZnCl_2$ or $BiCl_3$ yields 4 : 4′-*dihydroxy*-3 : 3′-*diacetyl*-1 : 1′-*dinaphthyl sulphide*, m.p. 200° [*diacetate* (**II**), m.p. 176°], nitrated in AcOH to 4 : 2 : 1-$NO_2{\cdot}C_{10}H_5Ac{\cdot}OH$; with S_2Cl_2 in Et_2O ($ZnCl_2$) (**I**) gives the corresponding *trisulphide*, m.p. 191—192°, acetylated to (**II**). β-$C_{10}H_7{\cdot}OH$ with SCl_2 or S_2Cl_2 ($ZnCl_2$) in Et_2O or C_6H_6 yields 2 : 2′-*dihydroxy*-1 : 1′-*dinaphthyl sulphide*, m.p. 212° (*diacetate*, m.p. 198°; brominated in AcOH to 1 : 2-$C_{10}H_6Br{\cdot}OH$), but with $SOCl_2$ gives no isolable product. In Et_2O ($ZnCl_2$), 1 : 2-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ with SCl_2 yields 4 : 4′-*dihydroxy*-3 : 3′-*dicarboxy*-1 : 1′-*dinaphthyl sulphide*, m.p. 265—267° [*diacetate* (**III**), m.p. 150—151°; *Ca* and *Ba* salts; nitrated to 2 : 4 : 1-$(NO_2)_2C_{10}H_5{\cdot}OH$], with S_2Cl_2 gives the corresponding *disulphide*, m.p. 259—260° [also acetylated to (**III**)], but does not react with $SOCl_2$. 2 : 3-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ with SCl_2 or S_2Cl_2 yields 2 : 2′-*dihydroxy*-3 : 3′-*dicarboxy*-1 : 1′-*dinaphthyl sulphide*, m.p. 285° [*diacetate*, m.p. 305—306°; *Ba* and *Ca* salts; nitrated to 4 : 3 : 2-$NO_2{\cdot}C_{10}H_5(OH){\cdot}CO_2H$], but does not react with $SOCl_2$. A. Lt.

Preparation of 22 : 23-dihydro-stigmasterol and -brassicasterol. E. Fernholz and W. L. Ruigh (*J. Amer. Chem. Soc.*, 1940, **62**, 3346—3348).—*Stigmasteryl*, m.p. 148—150°, $[\alpha]_D^{24}$ −47·1°, and *brassicasteryl* p-*toluenesulphonate*, m.p. 139·5—140·5°, $[\alpha]_D^{24}$ −61·0°, with KOAc in boiling abs. MeOH give i-*stigmasteryl*, m.p. 54—55°, $[\alpha]_D^{24}$ +34·7°, and i-*brassicasteryl Me ether*, m.p. 70—71°, $[\alpha]_D^{24}$ +20·0°, respectively. Hydrogenation (Pd-black; EtOAc) then gives oily H_2-ethers, which with $Zn(OAc)_2$ in boiling AcOH, followed by KOH–EtOH, afford 22 : 23-dihydro-stigmasterol, m.p. 135·5—136°, $[\alpha]_D^{24}$ −34·3° (digitonide; acetate, m.p. 118·5—119·5°, $[\alpha]_D$ −37°; 3 : 5-dinitrobenzoate, m.p. 201—202°, $[\alpha]_D^{24}$ −10·6°), and -*brassicasterol*, m.p. 157—158°, $[\alpha]_D^{24}$ −46·3° [*acetate*, m.p. 144—145°, $[\alpha]_D^{24}$ −45·5°; *benzoate*, m.p. 161—162°, $[\alpha]_D^{24}$ −19°; p-*nitro*-, m.p. (rapid heating) 172° and 243—244°, $[\alpha]_D^{24}$ −11·4°, and 3 : 5-*dinitro-benzoate*, m.p. 196·5—197·5°, $[\alpha]_D^{24}$ −17·1°]. *Stigmasteryl* 3 : 5-*dinitrobenzoate*, m.p. 226—228°, $[\alpha]_D^{24}$ −21·5°, is prepared. [α] are in $CHCl_3$. R. S. C.

Dehydration of 22-dihydrostigmasterol and cholesterol by iodine. T. Hasselstrom and B. L. Hampton (*J. Amer. Chem. Soc.*, 1941, **63**, 111—112).—Cholesterol and ~5% of I at 170—180° give *dicholesteryl ether* (8·5%), m.p. 198—199° (corr.), $[\alpha]_D$ −52° in $CHCl_3$ [*tetrabromide*, m.p. 178—179° (corr.)], and no unsaturated hydrocarbon. Crude sulphate pulp tallol and boiling H_2SO_4-MeOH give Me esters, b.p. 192—210°/6 mm., and a residue, which with 10% KOH gives 22-dihydrostigmasterol, m.p. 138—139°, $[\alpha]_D$ −21·5° in $CHCl_3$. With I at 160—170° this gives 4·7% of *di-22-dihydrostigmasteryl ether*, m.p. 182—183° (corr.), $[\alpha]_D$ −23° in $CHCl_3$ [*tetrabromide*, m.p. 164—166° (corr.)]. Unidentified iodides are formed as by-products in the above reactions. R. S. C.

Constituents of the adrenal cortex and related substances. XLIII. The fourth isomeric *allo*pregnane-3(β) : 17 : 20-triol. D. A. Prins and T. Reichstein (*Helv. Chim. Acta*, 1940, **23**, 1490—1501).—17-Formylandrostane-3(β) : 17(α)-diol diacetate, which according to its prep. from vinylandrostanediol has the α-configuration at $C_{(17)}$, is converted by an excess of MgMeBr followed by hydrolysis and re-acetylation into *allopregnane*-3(β) : 17(α) : 20(β)-*triol diacetate*, needles, m.p. 203—204°, or leaflets which are transformed into rodlets at 180° and subsequently melt at 202—204°, $[\alpha]_D^{16}$ −10·9°±2° in $CHCl_3$. The corresponding *triol*, m.p. 235—236° (frequently after transformation at 225°), $[\alpha]_D^{21}$ −8·7°±1·8°, $[\alpha]_{5461}^{21}$ −11·6°±1·8° in EtOH, is degraded by HIO_4 to MeCHO and *l*-androsterone. Since this has the α-configuration at $C_{(17)}$ it follows that substances *J* (**I**) and *O* have the 17(β) configuration. The isomeride giving a diacetate, m.p. 135°, has the 17(α) configuration. The two Δ⁵-pregnene-3(β) : 17 : 20-triols obtained by Butenandt *et al.* (A., 1939, II, 328) by hydroxylation of 3(β)-acetoxy-Δ⁵:¹⁷-pregnadiene differ in configuration at $C_{(17)}$ since that obtained in larger proportion (acetate, m.p. 159°) is hydrogenated to (**I**) and therefore belongs to the 17(β) series, whereas the other triol (acetate, m.p. 185°) gives the triol (**II**) and hence has 17(α) configuration.



(II.)

Substance *K* (**III**) is transformed by *p*-$C_6H_4Me{\cdot}SO_2Cl$ in anhyd. C_5H_5N into a non-homogeneous product, which is treated with NaI in $COMe_2$ and then hydrogenated (Raney Ni) in alkaline solution. Acetylation (Ac_2O in C_5H_5N) of this product does not appear to yield an *allo*pregnane-3(β) : 17 : 20-triol diacetate but a *substance*, $C_{25}H_{36(40)}O_5$, m.p. 193—195° after alteration at ~170°, $[\alpha]_D^{16}$ ±0·0° in $COMe_2$, also obtained when (**III**) or its triacetate is boiled for a short time with 7% aq. EtOH–HCl and then acetylated. A conversion of substance *P* into substance *L* could not be effected by similar reactions. H. W.

Synthetic anthelmintics. I. α-Substituted γ-butyrolactones. V. A. Vyas, K. V. Bokil, and K. S. Nargund (*J. Univ. Bombay*, 1940, **9**, Part 3, 145—149).—*β-Carbethoxy-α-phenylpropionic acid*, m.p. 96° (from the succinic anhydride and boiling EtOH), when reduced (Na + EtOH) and the product warmed with dil. H_2SO_4 yields α-phenyl-γ-butyrolactone, b.p. 170—172°/10 mm. (also prepared from $CH_2Ph{\cdot}CN$; Carré *et al.*, A., 1933, 392), hydrolysed to the γ-OH-acid, new m.p. 106°. Similarly *β-carbethoxy-α-p-*, m.p. 83°, and *-o-anisylpropionic acid*, an oil, yield α-p- (**I**) and -o-*anisyl-γ-butyrolactone* (**II**), b.p. 215—220°/25 mm. and 185—190°/17 mm., respectively, also synthesised via *β-cyano-β-p-* and *-o-anisylpropyl alcohol*, b.p. 135—140°/10 mm. and 127—129°/8 mm., respectively. (**I**) is hydrolysed (NaOH) to the *γ-OH-acid*, m.p. 88—89°, which reverts to (**I**) when kept at room temp. or warmed, but the OH-acid from (**II**) is unstable. *β-Carbethoxy-α-6-methoxy-*, m.p. 42°, and *-4-methoxy-m-tolylpropionic acid*, m.p. 102°, yield α-6-*methoxy-*, b.p. 200—210°/4 mm., and *-4-methoxy-m-tolyl-γ-butyrolactone*, m.p. 62°, b.p. 195—200°/12 mm., respectively; the latter is hydrolysed to the *γ-OH-acid*, m.p. 124° (from H_2O) or 114° (from C_6H_6). A. Lt.

Mechanism of elimination of water from organic compounds in the presence of bases. C. R. Hauser and D. S. Breslow (*J. Amer. Chem. Soc.*, 1940, **62**, 3344—3346).—H_2O is eliminated from alcohols by bases if the H on $C_{(\beta)}$ is sufficiently activated. A reaction mechanism is postulated. OH·CHPh·$CH_2{\cdot}CO_2Et$ and $NaCPh_3$ in Et_2O give CHPh:CH·CO_2Et and some CHPh:CH·CO_2H (20% in all). NaOEt in Et_2O is more effective, giving 75% in all. $CH_2Ph{\cdot}CHPh{\cdot}OH$ is unaffected by $NaNH_2$ in liquid NH_3. R. S. C.

Alkamine esters of 4-acetylferulic and 3 : 4-dimethoxycinnamic acid. L. S. Fosdick and A. C. Starke, jun. (*J. Amer. Chem. Soc.*, 1940, **62**, 3352—3355).—Methylation (Me_2SO_4–NaOH) of 4 : 3 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CH{:}CH{\cdot}CO_2H$ and hydrolysis of the resulting ester gives 4 : 3 : 1-$(OMe)_2C_6H_3{\cdot}CH{:}CH{\cdot}CO_2H$, the acid *chloride* (prep. by $SOCl_2$), m.p. 80—82°, of which with $NR_2{\cdot}[CH_2]_n{\cdot}OH$ in C_6H_6 gives *β-di-ethyl-* (**I**), m.p. 162—163°, *-n-propyl-*, m.p. 124—127°, and *-n-butyl-aminoethyl*, m.p. 116—117°, *γ-di-ethyl-*, m.p. 142—144°, *-n-propyl-*, m.p. 138—139°, and *-n-butyl-aminopropyl*, m.p. 98—99°, 3 : 4-*dimethoxycinnamate hydrochlorides*. 4 : 3 : 1-$OAc{\cdot}C_6H_3(OMe){\cdot}CH{:}CH{\cdot}COCl$, m.p. 133—134°, similarly gives *β-di-ethyl-* (**II**), m.p. 185—186°, *-n-propyl-*, m.p. 178—179·5°, and *-n-butyl-aminoethyl*, m.p. 193·5—195°, *γ-di-ethyl-*, m.p. 155—157°, *-n-propyl-*, m.p. 153—154°, and *-n-butyl-aminopropyl*, m.p. 148—149°, 4-*acetylferulate hydrochlorides*. (**I**) and (**II**) are as potent as procaine as local anæsthetics, but are as toxic as cocaine. R. S. C.

Correlation of configurations of α-aminophenylacetic acid and of alanine. M. Kuna, G. Ovakimian, and P. A. Levene (*J. Biol. Chem.*, 1941, **137**, 337—342; cf. A., 1940, II, 328).—Reduction (H_2, PtO_2, AcOH, room temp.) of $NH_2{\cdot}CHPh{\cdot}CH_2{\cdot}OH$ (**I**), $[\alpha]_D^{25}$ −15° in MeOH, gives *β-acetamido-β-*cyclo*hexylethanol*, $[\alpha]_D^{25}$ ±0° in MeOH, 5·2° in $CHCl_3$, and *β-amino-β-*cyclo*hexylethyl acetate*, $[\alpha]_D^{25}$ −7·6° in $CHCl_3$. The latter is reduced by AcOH–HI at 125° to α-*cyclo*hexylethylamine (*hydrochloride*, $[\alpha]_{5461}^{25}$ −3·1° in H_2O). Similar hydrogenation of $NH_2{\cdot}CHPh{\cdot}CO_2Et$, $[\alpha]_D^{25}$ −113° (homogene-

ous), gives *Et α-acetamido-α-cyclohexylacetate*, m.p. 73—75°, $[\alpha]_D^{25}$ +4·6° in MeOH, which is unaffected by H_2 (Raney Ni) at 160 atm. and 75° for 9 hr. (**I**) with keten in MeOH yields ON-*diacetyl-β-amino-β-phenylethanol* (**II**), $[\alpha]_D^{25}$ −32·1°, $[M]_D$ −71° in MeOH, hydrolysed (MeOH + 0·5N-NaOH) to *β-acetamido-β-phenylethanol*, $[\alpha]_{5461}^{25}$ −46·7° in $CHCl_3$. Hydrogenation (PtO_2) of (**II**) in AcOH at room temp. yields ON-*diacetyl-β-amino-β-cyclohexylethanol*, $[\alpha]_{5461}^{25}$ +16·7° in $CHCl_3$. The results show that *d*(−)-NH_2·CHPh·CO_2H is correlated to *d*(−)-alanine in agreement with Reihlen *et al.* (A., 1938, II, 265). J. N. A.

Dipeptides of β-amino-acids. II. Derivatives of β-phenyl-β-alanine. (Miss) E. Dyer (*J. Amer. Chem. Soc.*, 1941, **63**, 265—267; cf. A., 1937, II, 448).—$ClCO_2$·CH_2Ph and NH_2·CHPh·CH_2·CO_2H (*hydrobromide*, m.p. 182—183°) in N-NaOH at 7—15° give *N-carbobenzyloxy-β-phenyl-β-alanine* (30%), m.p. 126—127·5°, converted by PCl_5 in Et_2O at 0° and later room temp. into the chloride, which with NH_2·CH_2·CO_2Et or CH_2Ph·CH(NH_2)·CO_2Et in EtOAc gives *N′-carbobenzyloxy-β′-phenyl-β′-alanyl-glycine Et* ester, m.p. 123—133°, and *-β-phenyl-α-alanine Et* ester, m.p. 142—144°, respectively. Alkaline hydrolysis then gives *N′-carbobenzyloxy-β′-phenyl-β′-alanyl-glycine*, m.p. 190·5—191·5° (gas), and *-β-phenyl-α-alanine*, m.p. 190—192° (decomp.), hydrogenated to PhMe and *β′-phenyl-β′-alanyl-glycine*, +H_2O, decomp. 245° (rapid heating), and *-β-phenyl-α-alanine*, m.p. 263—264° (decomp.), respectively.

CH_2Ph·O·CO·NH·CH(CH_2Ph)·CO_2H with PCl_5–Et_2O gives 2 : 5-diketo-4-benzyltetrahydro-oxazole (45%), m.p. 128°. The azlactone from NHAc·CH(CH_2Ph)·CO_2H with NH_2·CHPh·CH_2·CO_2Et (hydrochloride, m.p. 137—138°) in Et_2O gives *N′-acetyl-β′-phenyl-*, m.p. 195—196°, and thence *β′-phenyl-*, m.p. 232—233° (decomp.) [*hydrobromide*, m.p. 212—213° (decomp.)], *-α′-alanyl-β-phenyl-β-alanine*. M.p. are corr. R. S. C.

Stability of perbenzoic acid prepared without the use of alkali-metal alkoxides. H. N. Calderwood and L. W. Lane (*J. Physical Chem.*, 1941, **45**, 108—111).—BzO_2H prepared substantially by the method of Brooks *et al.* (cf. A., 1933, 1291) is stable when dissolved in carefully washed $CHCl_3$ and stored at 6° in a vessel containing anhyd. Na_2SO_4. Explanations of the instability of BzO_2H are reviewed but the authors were unable to identify the impurities in the $CHCl_3$ (removal of which increased the stability). C. R. H.

Condensation of carbamide with resorcinol. J. J. Roemer and W. M. Degnan (*J. Amer. Chem. Soc.*, 1941, **63**, 103—105). —*m*-$C_6H_4(OH)_2$ (**I**), $CO(NH_2)_2$, and $ZnCl_2$ at 132° give 34—41% of *β*-resorcylamide (**II**), new m.p. 228—229°, obtained also from KCNO (27%) (thus elucidating the mechanism of the reaction), NHMe·CO·NH_2 (28·4%), and NO_2·NH·CO·NH_2 (22·5%), but not from CN·NH_2; NH_2·CO_2Et affords 0·5% of (**II**). PhNCO, (**I**), and $ZnCl_2$ at 128—132° give only the di(phenylurethane). R. S. C.

Reduction products of chloral-hydroxybenzoic acids. H. V. Dharwarkar and R. L. Alimchandani (*J. Univ. Bombay*, 1940, **9**, Part 3, 163—169; cf. Meldrum *et al.*, A., 1935, 748).—2 : 1 : 5-OH·C_6H_3(CO_2H)·CH(OH)·CCl_3 is reduced (Zn dust, AcOH) to 2-hydroxy-5-*ββ*-dichlorovinylbenzoic acid (**I**) (Calvet *et al.*, A., 1936, 844) (*acetate*, m.p. 126°; *benzoate*, m.p. 140°), hydrolysed (conc. H_2SO_4 at 75—80°) to *4-hydroxy-5-carboxyphenylacetic acid*, m.p. 207—208° (*Ag* salt), also obtained by demethylating (HI) 2 : 1 : 5-OMe·C_6H_3(CO_2H)·CH_2·CO_2H. Methylation (Me_2SO_4) of (**I**) gives a compound [identical with the reduction product of 2 : 1 : 5-OMe·C_6H_3(CO_2H)·CH(OH)·CCl_3 (Hurry *et al.*, A., 1934, 1216)], which with boiling 10% NaOH yields *β-chloro-α-4-methoxy-3-carboxyphenylacetylene*, m.p. 175°, converted by HCl in $CHCl_3$ into *2-methoxy-5-αβ-dichlorovinylbenzoic acid*, m.p. 145°. 6-Carboxy-2 : 4-bistrichloromethyl-1 : 3-benzdioxin (Chattaway *et al.*, A., 1927, 458) is similarly reduced to *4-hydroxy-5-ββ-dichlorovinylbenzoic acid* (**II**), m.p. 171—172° (*acetate*, m.p. 191—192°), hydrolysed (conc. H_2SO_4 at 70—80°) to *2-hydroxy-5-carboxyphenylacetic acid* (**III**), m.p. 186° (decomp.) (*Ag* salt), also obtained by demethylating (HI) the *2-OMe-acid*, m.p. 264—265° (*Ag* salt), prepared from 4 : 1 : 5-OMe·C_6H_3(CO_2H)·CH(OH)·CCl_3 via 4-methoxy-5-*ββ*-dichlorovinylbenzoic acid, new m.p. 226—227°. *β-Chloro-α-2-methoxy-5-carboxyphenylacetylene* has m.p. 219—220°. (**III**) at 195—200° yields *1-keto-1 : 2-dihydrocoumarone-4-carboxylic acid*, m.p. 232—233° (*Ag* salt). 5-Hydroxytrichloromethylphthalide is reduced to 3-hydroxy-6-*ββ*-dichlorovinylbenzoic acid (**IV**), new m.p. 196—197° (*acetate*, m.p. 170—171°), hydrolysed (conc. H_2SO_4 at 34°) to *4-hydroxy-6-carboxyphenylacetic acid*, m.p. 215° (decomp.) (*Ag* salt). Methylation (Me_2SO_4) of (**IV**) gives a compound identical with the reduction product, new m.p. 167—168° (*loc. cit.*), of 5-methoxytrichloromethylphthalide. With 50% NaOH, (**I**) yields a tar, (**II**) yields *1-chlorocoumarone-4-carboxylic acid*, m.p. 242—243° (*Ca* salt +5H_2O), and (**IV**) yields a *compound*, m.p. 215° (decomp.). (**I**), (**II**), and (**IV**) give no addition products with dry HCl or Br. A. Lr.

Local anæsthetics in the naphthalene series. F. F. Blicke, H. C. Parke, and E. L. Jenner (*J. Amer. Chem. Soc.*, 1940, **62**, 3316—3319).—The following are prepared from the appropriate NO_2·$C_{10}H_6$·COCl (for the amides, in C_6H_6), subsequent reduction being effected by $SnCl_2$–HCl–AcOH or H_2–Raney Ni–EtOH at 3·5 atm. *β-Diethylaminoethyl*, m.p. 204—205°, *γ-diethylamino-n-propyl*, m.p. 194—196°, and *γ-diethylamino-ββ-dimethyl-n-propyl 5-nitro-2-naphthoate hydrochloride*, m.p. 107—109°, *β-β′-diethyl-*, m.p. 112—113°, and *β-β′-di-n-butylaminoethoxyethyl 4-nitro-1-naphthoate hydrochloride*, m.p. 97—98°, *β-β′-diethyl-*, m.p. 173—175°, and *β-β′-di-n-butyl-aminoethoxyethyl 5-nitro-1-naphthoate hydrochloride*, m.p. 113—115°, and the corresponding *aminonaphthoate hydrochlorides*, m.p. 207—208°, 156—158°, 190—192°, 113—115°, 135—136°, 118—120°, and 114—116°, respectively; *β-dibutylaminoisopropyl 4-amino-1-naphthoate hydrochloride*, m.p. 178—179°; *3-nitro-*, m.p. 167—169°, *4-nitro-*, m.p. 152—154°, and *4-amino-1-naphtho-β-diethylaminoethylamide hydrochloride*, m.p. 175—177°; *4-nitro-*, m.p. 152—154°, and *4-amino-1-naphtho-γ-diethylaminopropylamide hydrochloride*, m.p. 198—200°; *4-nitro-*, m.p. 178—180°, and *4-amino-1-naphtho-γ-piperidinopropylamide hydrochloride*, m.p. 205—207°; *p-nitrobenz-*, m.p. 223—224° (free base, m.p. 120—121°), *4-nitro-1-naphtho-*, m.p. 223—224° (free base, m.p. 129—131°), and *4-amino-1-naphtho-β-morpholinoethylamide hydrochloride*, m.p. 239—242°; *p*-aminobenzethylamide, m.p. 155—158° (*hydrochloride*, m.p. 209—210°). These products are anæsthetics, the esters being more potent than the amides. NEt(·$[CH_2]_2$·OH)$_2$ and *p*-NO_2·C_6H_4·COCl in boiling C_6H_6 give ethyldi-*β-p*-nitro-, m.p. 120—121° (*hydrochloride*, m.p. 178—179°), reduced ($SnCl_2$–HCl–AcOH) to ethyldi-*β-p*-amino-benzoyloxyethylamine, m.p. 99—101° (*hydrochloride*, m.p. 199—201°, a weak anæsthetic). Prep. of the following is described: *β-β′*-diethyl-, b.p. 101—105°/9 mm., and *-di-n*-butyl-aminoethoxyethyl alcohol, b.p. 142—144°/11 mm., from OH·$[CH_2]$·O·$[CH_2]_2$·Cl; *γ*-piperidino-*n*-propylamine, b.p. 201—203°/740 mm., from *o*-$C_6H_4(CO)_2N$·$[CH_2]_3$·Br; 5 : 2-NO_2·$C_{10}H_6$·CN, m.p. 164—167°; 5 : 2-NO_2·$C_{10}H_6$·CO_2H, m.p. 291—293° (*chloride*, m.p. 126—128°, b.p. 223—224°/13 mm.). NEt_2·$[CH_2]_2$·NH_2 and NEt_2·$[CH_2]_3$·NH_2 boil at 143—144° and 164—166°, respectively. R. S. C.

Methoxytolylsuccinic acids. V. A. Vyas, K. V. Bokil, and K. S. Nargund (*J. Univ. Bombay*, 1940, **9**, Part 3, 140—144). —4 : 3 : 1-OMe·C_6H_3Me·CHO with CN·CH_2·CO_2Na yields *α-cyano-β-(6-methoxy-m-tolyl)acrylic acid*, m.p. 217° (*Me* ester, m.p. 153—154°), the *Et* ester, m.p. 117°, of which with HCN followed by boiling 25% HCl affords *6-methoxy-m-tolylsuccinic acid*, m.p. 192° [*Me*, m.p. 75°, and *Et* ester, b.p. 175—180°/8 mm.; *anhydride* (from the acid and AcCl), m.p. 80°; *monoanilide*, m.p. 168°, and *-p-toluidide*, m.p. 127°]. The corresponding *5-methoxy-o-tolyl* compounds have m.p. 225°, 118°, 93—94°, 196°, 160°/3 mm. (b.p.), 165°/5 mm. (b.p.), 205—210°/8 mm. (b.p.), 156°, and 162°, and the *4-methoxy-m-tolyl* compounds, 228°, 134°, 83°, 186°, —, —, 119°, 154°, and 197°, respectively. A. Lr.

Derivatives of *cyclo*hexane. Synthesis of 1-carboxy*cyclo*hexane-1-succinic, -1-α-propionic, and -1-α-benzylacetic acids, and of α-*cyclo*hexylsuccinic acids. R. D. Desai and G. S. Sahariya (*J. Univ. Bombay*, 1940, **9**, Part 3, 107—114).—The product (**I**) from CN·CHNa·CO_2Et (**II**) and *cyclo*hexanone cyanohydrin in EtOH, with CH_2Br·CO_2Et yields 1-cyano-1-*cyclo*hexylacetonitrile and Et_2 1-cyano*cyclo*hexane-1-α-cyanosuccinate, b.p. 202—204°/2 mm., m.p. 74° (cf. Chatterjee, A., 1937, II, 377), hydrolysed (conc. H_2SO_4 at room temp., then diluted and boiled) to 1-carboxy*cyclo*hexane-1-succinic acid, new m.p. 206° (efferv.) (cf. *loc. cit.*) [anhydride (viscid liquid); *anilic acid* (from the anhydride and NH_2Ph in C_6H_6), m.p. 132°; *anil anilide* (from the acid and NH_2Ph at 170—175°), m.p. 167°; *tolil toluidide*, m.p. 161—162°; *imide*, m.p. 125—126°]. (**I**) with CH_2PhCl yields *Et* 1-*cyano*cyclo*hexane*-1-α-

benzylcyanoacetate, b.p. 220°/8 mm., m.p. 115°, hydrolysed (conc. H_2SO_4) to the *diamide*, m.p. 215°, or (conc. H_2SO_4, then diluted and boiled) to 1-*carboxy*cyclo*hexane*-1-*α-benzylacetic acid*, m.p. 195° [*anhydride*, m.p. 104°; *anilic acid* (+$3H_2O$), m.p. 177°; *imide*, m.p. 175°]. (I) with MeI (NaOEt) yields *Et* 1-*cyano*cyclo*hexane*-1-*α-cyanopropionate*, b.p. 169°/6 mm., m.p. 52—54°, hydrolysed to 1-carboxy*cyclo*hexane-1-α-propionic acid, m.p. 125° (cf. Kandiah, A., 1932, 614) [anhydride (liquid); anilic acid, new m.p. 171—172°; *p-toluidinic acid*, m.p. 176°; *imide*, m.p. 102°]. (II) with *cyclo*hexyl bromide yields Et *cyclo*hexylcyanoacetate (III), b.p. 148—150°/20 mm., hydrolysed (EtOH–KOH) to *cyclo*hexylmalonic acid (*di*-p-*toluidide*, m.p. 128—129°) and some α-*cyanodicyclohexylacetic acid* (?), m.p. 200°. (III) with NaOEt, then $CH_2Br{\cdot}CO_2Et$ in EtOH, yields *Et*$_2$ α-*cyano*-α-cyclo*hexylsuccinate*, b.p. 195—198°/18 mm., hydrolysed to *cyclo*hexylsuccinic acid, m.p. 150° (cf. Ranganathan, A., 1939, II, 321) (anhydride, m.p. 41—42°; *anilic acid*, m.p. 192°; *imide*, m.p. 164°). None of these acids shows signs of isomerism. A. LI.

Stereochemistry of diphenyls. LI. Resolution of diphenic acids having many-membered bridges across the 5 : 5′-positions. Novel type of restricted rotation. R. Adams and N. Kornblum (*J. Amer. Chem. Soc.*, 1941, **63**, 188—200; cf. A., 1940, II, 345).—When the 5 : 5′-positions of diphenic acid are bridged by $O{\cdot}[CH_2]_n{\cdot}O$, there are three possibilities. (1) The bridge-chain is not long enough to permit existence of the acid with *trans*-CO_2H; the *cis*-acid exists in two enantiomorphic forms, which can racemise only if the CO_2H slip past each other; the C_6H_6 rings are inclined at an angle to each other; if, however, the bridge-chain is very short, the strain may cause the C_6H_6 rings to become non-coaxial, so that the CO_2H have room to lie in one plane and the mol. becomes symmetrical and non-resolvable. (2) The bridge-chain is long enough to permit the Ph_2 nucleus to rotate freely within it and isomerism is impossible. (3) A bridge-chain of intermediate length excludes rotation envisaged in case 2 but permits existence of two *cis*- and two *trans*-forms, of which *cis*-form *a* may be in equilibrium with *trans*-form *a* and *cis*-form *b* with *trans*-form *b*. Stuart models indicate that case 3 exists if $n = 10$, and with some distortion of the *trans*-form if $n = 8$, that case 1 exists if $n = 7$ or 6, that the C_6H_6 rings cease to be coaxial if $n = 5$, and that for case 2, n must be 50—100. These predictions are verified for $n = 10$ and 8. The octa- and deca-methylenedioxy-acids have half life periods 1995 and 1491 min. at 23° and 170 and 120 min. at 43° in dioxan, and 19·1 and 22 min., respectively, in 0·476N-NaOH at 34·5°. The greater stability of the former acid is probably due to the shorter bridge allowing less vigorous oscillations of the C_6H_6 nuclei about their common linking and thus less slipping of the CO_2H.

o-Dianisidine and *o*-tolidine are deaminated in good yield by adding acid tetrazonium solutions to 30% aq. H_3PO_2. Addition of KOH–EtOH (0·45) to (3 : 1-$OH{\cdot}C_6H_4$)$_2$ (1 mol.), new m.p. 125·5—126° [prep. from (3 : 1-$OMe{\cdot}C_6H_4$)$_2$, forms, m.p. 42—43·5° and 34—35°], and $Br{\cdot}[CH_2]_{10}{\cdot}Br$ (6·8 mols.) in boiling abs. EtOH gives 3-*hydroxy*-3′-*κ-bromo*-n-*decyloxydiphenyl* (I) (30—40%), m.p. 51·5—52·5°, and a little 3 : 3′-*di-κ-bromo*-n-*decyloxydiphenyl*, m.p. 86—87°. Addition of (I) in *iso*-$C_5H_{11}{\cdot}OH$ to K_2CO_3 in *iso*-$C_5H_{11}{\cdot}OH$ in a high-dilution apparatus (detailed and modified) gives 70% of 3 : 3′-*decamethylenedioxydiphenyl*, m.p. 116·5—117·5°, the structure of which is demonstrated by failure to react with H_2–PtO_2, $KMnO_4$, or MgEtBr, and by insolubility in alkali. Prep. of 3 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}OH$, m.p. 32—33°, is modified to give a 73—77% yield. Reduction of 3 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}OMe$, b.p. 148—150°/3 mm., by Zn dust–aq. EtOH–NaOH and rearrangement of the resulting hydrazo-compound gives 33—39% of 4 : 4′-*diamino*-5 : 5′-*dimethoxy*-2 : 2′-*dimethyldiphenyl*, m.p. 155—156°, and a little 2 : 2′-*dimethoxy*-5 : 5′-*dimethylazobenzene*, m.p. 174—175°. Tetrazotisation of the diamine and treatment with H_3PO_2 gives 5 : 5′-*dimethoxy*-2 : 2′-*dimethyldiphenyl* (80—85%), m.p. 56·5—57·5°, which with boiling 57% HI gives (5 : 2 : 1-$OH{\cdot}C_6H_3Me{\cdot}$)$_2$ (II), softens at 228°, m.p. 235—236° (lit. 229°), and is oxidised by $KMnO_4$ to [2 : 5 : 1-$CO_2H{\cdot}C_6H_3(OMe){\cdot}$]$_2$, softens at 213°, m.p. 231—233° (lit. 234°). With $Br{\cdot}[CH_2]_{10}{\cdot}Br$ and KOH–EtOH, (II) gives 60—68% of 5-*hydroxy*-5′-*κ-bromodecyloxy*-2 : 2′-*dimethyldiphenyl*, m.p. 42—44°, which (as above) yields 5 : 5′-*decamethylenedioxy*-2 : 2′-*dimethyldiphenyl* (III) (76%), *forms*, m.p. 110—111° and 85—85·5°. Addition of solid $KMnO_4$ to (III) in C_5H_5N–H_2O at 100° (not other methods) gives 20% of 5 : 5′-*decamethylenedioxy-diphenic* (IV), m.p. 285—290° (decomp.; bath preheated at 250°), and 2′-*methyldiphenyl*-2-*carboxylic acid*, softens at 155°, m.p. 163—165°. Resolution of (IV) by brucine in MeOH gives the d-*acid*, m.p. 280—290° (decomp.), $[\alpha]_D^{23}$ +112° in dioxan [*dibrucine* salt, +4MeOH, m.p. 155—163°, $[\alpha]_D^{20}$ −55·8° → −33° (after 30 hr.) in $CHCl_3$]. $OH{\cdot}[CH_2]_8{\cdot}OH$, b.p. 154—156°/12 mm., prepared in 90% yield from Et_2 suberate by H_2–Cu chromite at 250°/6000 lb., is converted by HBr at 90—95°, later 140°, into the dibromide (75%), b.p. 118—120°/2 mm. This gives (methods as above) 5-*hydroxy*-5′-*θ-bromo-octyloxy*-2 : 2′-*dimethyldiphenyl* (58—66%), m.p. < room temp. (and some cryst. diether), 5 : 5′-*octamethylenedioxy*-2 : 2′-*dimethyldiphenyl* (48%), m.p. 76—77·5°, dl- (23%), m.p. 344° (decomp.; block) [*brucine* salt, softens at 175°, m.p. 187° (gas), $[\alpha]_D^{20}$ +1·16° in $CHCl_3$], and l-5 : 5′-*octamethylenedioxydiphenic acid*, m.p. 344° (block, $[\alpha]_D^{23}$ −212° in dioxan [*dicinchonine* salt, m.p. 155—170° according to the rate of heating, $[\alpha]_D^{27}$ −171° → −155° (after 60 hr.) in $CHCl_3$]. M.p. are corr. R. S. C.

Reactions of aldehydes with amines. II. New aldehyde reagent. F. G. Singleton and C. B. Pollard (*J. Amer. Chem. Soc.*, 1941, **63**, 240—242; cf. A., 1940, II, 374).—*m*-$NO_2{\cdot}C_6H_4{\cdot}N(CH_2Ph)_2$ (prep. from *m*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, CH_2PhCl, NaOAc, and a little I at 125—130°) with mossy Zn in conc. HCl–EtOH gives *m*-$NH_2{\cdot}C_6H_4{\cdot}NH(CH_2Ph)_2$ (I), m.p. 101° (cf. Desai, A., 1928, 1237). With ArCHO (Ar = Ph, *o*-$OH{\cdot}C_6H_4{\cdot}$, $CHPh{:}CH{\cdot}$, *p*-$C_6H_4Cl{\cdot}$, *o*- or *p*-$OMe{\cdot}C_6H_4{\cdot}$), (I) gives yellow, amorphous *Schiff's bases*, m.p. gradual, <100°, which in Et_2O–HCl give blood-red, resinous mono- and then colourless, unstable di-hydrochlorides. The dihydrochlorides in cold H_2O regenerate ArCHO and (I). 1% of (I) in 95% EtOH containing 10 c.c. of conc. HCl per l. serves as a reagent for aldehydes: with saturated aliphatic and arylaliphatic aldehydes it gives a red colour, followed in ⩾10 min. by a green fluorescence; with unsaturated aliphatic aldehydes the initial red colour is darker and a dull brownish-green fluorescence follows in ⩾10 min.; aromatic aldehydes give bright yellow to dark red colours, followed by a green fluorescence after ⩽2 hr. The limit of sensitivity is ~0·002%. 44 examples are cited and the following exceptions are noted. CH_2O gives a yellow colour and no fluorescence. $CHMe{:}CH{\cdot}CH{:}CH{\cdot}CHO$, $CHPh{:}CH{\cdot}CHO$, and nitro-aryl aldehydes give no fluorescence. Furfuraldehyde gives a red colour, changing slowly to green. Chloral gives no colour or fluorescence. The fluorescence is probably due to formation of acridines. R. S. C.

Production of vanillin from waste sulphite liquor.—See B., 1941, II, 75.

Oxidation potentials of ketones and an aldehyde.—See A., 1941, I, 117.

Addition reactions of α-keto-acids. VII. (Misses) M. Reimer and A. L. Morrison (*J. Amer. Chem. Soc.*, 1941, **63**, 236—240).—*β-Bromo-α-keto-γ*-p-*phenetyl-Δ*$^{\beta}$*-butenoic acid* resembles the *p*-anisyl-acid (cf. A., 1940, II, 374) in existing in colourless chelated (I) and yellow unchelated (II) *forms*. Addition of 1·8 mols. of 25% KOH–EtOH to 1 mol. each of $AcCO_2H$ and *p*-$OEt{\cdot}C_6H_4{\cdot}CHO$ (prep. from *p*-$OH{\cdot}C_6H_4{\cdot}CHO$ by EtBr–KOH–EtOH) gives *α-keto-γ*-p-*phenetyl-Δ*$^{\beta}$*-butenoic acid* (III) (85—93%), yellow, m.p. (+*x*C_6H_6) 47°, (solvent-free) 89—90° (*Me*, m.p. 79°, and *Et* ester, m.p. 41—42°, yellow; *K* salt), oxidised by H_2O_2–NaOH to *p*-$OEt{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$. In $CHCl_3$, (II) gives a *dibromide* (IV), m.p. 140—143° (decomp.) after sintering [rapidly loses HBr; *Me* ester (V), m.p. 101—102°], converted by boiling H_2O into (I), m.p. 148—149° [colourless *Na* salt (VI)], which with CH_2N_2 or $CHEtN_2$ gives a colourless *Me*, m.p. 85—86°, or *Et* ester, m.p. 80—81°, but with boiling HCl–MeOH or –EtOH gives a yellow *Me* (VII), m.p. 75—76°, or *Et* ester, m.p. 55—56°. Addition of acid to an aged solution of (I) in aq. Na_2CO_3 gives (II) [yellow *Na* salt (VIII)], which at 60° regenerates (I). With CH_2N_2, (II) gives (VII). (IV) is unstable, but solid (V) is stable; in warm H_2O, (V) gives (I) and (VII). H_2O_2 does not affect (VI), but converts (VIII) into *α-bromo*-p-*ethoxycinnamic acid*, m.p. 180—181° (*Me* ester, m.p. 51—52°). R. S. C.

Synthesis of γ-ketobutyric acids with anisyl or methoxytolyl groups as substituents in the α- and γ-positions. B. S. Mehta, K. V. Bokil, and K. S. Nargund (*J. Univ. Bombay*,

1940, **9**, Part 3, 156—162).—*β-p*-Methoxybenzoylacrylic acid (**I**) in 80% H_2SO_4 at room temp. with the appropriate aryl Me ethers gives the following α-substituted *β*-p-*methoxybenzoylpropionic acids* in 12—92% yields: 6-*methoxy*-m-, m.p. 179° (*Ag* salt), 5-*methoxy*-o-, m.p. 132° (*Ag* salt), and 4-*methoxy*-m-*tolyl*-, m.p. 140—141°, 3 : 4-, m.p. 180°, and 2 : 4-*dimethoxyphenyl*-, m.p. 128°, *p*-anisyl-, and 4-, m.p. 151—152° (*Me*, m.p. 106°, and *Et* ester, m.p. 110°), and 2-*methoxy*-1-*naphthyl*-, m.p. 120—125°. The first five acids are synthesised as follows: *p*-OMe·C_6H_4·COMe with the appropriate ArCHO and EtOH–NaOH yields p-*anisyl* 4-*methoxy*-3-*methylstyryl*, m.p. 86° [*dibromide*, m.p. 122° (decomp.)], 4-*methoxy*-2-*methylstyryl*, m.p. 117—118° [*dibromide*, m.p. 116° (decomp.)], 2-*methoxy*-5-*methylstyryl*, m.p. 102—103° (non-cryst. *dibromide*), 3 : 4-*dimethoxystyryl*, m.p. 96—98°, and 2 : 4-*dimethoxystyryl ketone*, m.p. 82°, which with aq. EtOH–KCN followed by AcOH and then boiling dil. H_2SO_4 give the required acids. The last two acids could not be so synthesised. All these acids with *o*-OH·C_6H_4·CHO and piperonal give pyrylium and (gummy) piperonylidene derivatives respectively. *p*-$C_6H_4(OMe)_2$ and *m*-OH·C_6H_4·OMe give no cryst. products with (**I**). Conc. H_2SO_4 at 35° sulphonates (**I**). Condensation could not be effected with $AlCl_3$ or dry HCl. A. Li.

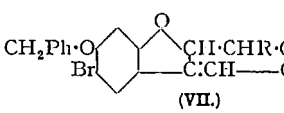
β-Arylglutaconic acids. VI. *C*-Benzoylation of *β*-arylglutaconic anhydrides and thermal decomposition of *C*-acyl-*β*-arylglutaconic anhydrides. G. R. Gogte (*J. Univ. Bombay*, 1940, **9**, Part 3, 127—139).—*β-p*-Anisylglutaconic anhydride (**I**) with BzCl in C_5H_5N yields the *α-Bz* derivative (**II**), m.p. 119° (decomp.), which gives a dark green coloration with $FeCl_3$–EtOH and yields (**I**) (as acid) and BzOH when heated with EtOH, then 10% NaOH. (**II**) with N-NaOH at 100° yields *γ-benzoyl-β-p-anisyl-*Δ^{α}*-butenoic acid*, m.p. 114° (decomp.) [*semicarbazone*, m.p. 162° (decomp.)], the *lactone*, m.p. 145°, of which [obtained by heating the acid or (**II**) with HCl or by heating (**II**) at 120°/50 mm.] reverts to the acid with EtOH–NaOH. This acid when heated gives an oil which yields a semicarbazone, m.p. 142° (decomp.). Further benzoylation of (**II**) gives the *αγ-Bz*$_2$ derivative (**III**), m.p. 194° (decomp.), which when heated at 200°/40 mm. gives a *compound*, $C_{25}H_{18}O_4$, m.p. 193°, hydrolysed by EtOH–NaOH to *αγ-dibenzoyl-β-p-anisylpropylene*, m.p. 124°, also obtained from (**III**) and aq. NaOH. *α-Benzoyl-β-(2-methoxy-5-methylphenyl)glutaconic anhydride* (**IV**) [prep. as (**II**)], m.p. 158° (decomp.), gives a blue colour with EtOH–$FeCl_3$, and when heated with alkali gives an acid converted by HCl into the *lactone*, m.p. 126°, also obtained by heating (**IV**). *αγ*-Diacetyl-*p*-anisylglutaconic anhydride when heated at 150—160°/50 mm. yields the *lactone*, *p*-OMe·C_6H_4·C<CAc–CO / CH:CMe>O, m.p. 111°, converted by boiling 10% NaOH into 3′-hydroxy-4-methoxy-5′-methyldiphenyl and its -6′-*carboxylic acid*, m.p. 182° (previously termed the -2′-carboxylic acid; A., 1940, II, 133). Similarly *αγ*-diacetyl-*β*-(2-methoxy-5-methylphenyl)glutaconic anhydride at 180°/40 mm. yields an analogous *lactone*, m.p. 164°, and thence 3′-hydroxy-2-methoxy-5 : 5′-dimethyldiphenyl and its -6′-*carboxylic acid*, m.p. 213° (decomp.) (cf. *loc. cit.*). (**I**) with *p*-C_6H_4Br·COCl in C_5H_5N yields the α-p-*bromobenzoyl* derivative (**V**), m.p. 145° (decomp.), which gives a violet coloration with $FeCl_3$, and with boiling EtOH, then 10% aq. NaOH, yields the glutaconic acid and *p*-C_6H_4Br·CO_2H. (**V**) with warm 5% NaOH yields *γ-p-bromobenzoyl-β-p-anisyl-*Δ^{α}*-butenoic acid* (**VI**), m.p. 123° (decomp.) [semicarbazone, m.p. 174° (decomp.)], decarboxylated (heat or hot alkali) to a *ketone* (**VII**), m.p. 115°. (**V**) when heated at 150—160°/150 mm. yields the *lactone*, m.p. 208°, of (**VI**) [also obtained from (**V**) and boiling aq. HCl or (**VI**) with EtOH–HCl], which with boiling 5% EtOH–NaOH gives (**VII**), and a small amount of (**VI**). Benzoylation of (**V**) affords *γ-benzoyl-α-p-bromobenzoyl-β-p-anisylglutaconic anhydride*, m.p. 164° (decomp.), also obtained from (**II**) and *p*-C_6H_4Br·COCl. A. Li.

Condensation of *o*-anisylsuccinic anhydride with phenyl methyl ethers. G. S. Savkar, K. V. Bokil, and K. S. Nargund (*J. Univ. Bombay*, 1940, **9**, Part 3, 150—155).—*o*-Anisylsuccinic anhydride with aryl Me ethers and $AlCl_3$ in $PhNO_2$ or $C_2H_2Cl_4$ (cf. A., 1940, II, 132) gives substituted benzoyl-α-*o*-anisylpropionic acids. *β-p-Methoxy*-, m.p. 140° (*Me*, m.p. 83°, and *Et* ester, m.p. 96°; *Ag* salt), and -3 : 4-, m.p. 127° (*Me*, m.p. 107°, and *Et* ester, m.p. 75°), -2 : 4- (**I**), m.p. 162° (*Et* ester, m.p. 97°), and -2 : 5-*dimethoxy-benzoyl-α-o-anisylpropionic acid*, m.p. 141° (*Me*, m.p. 110°, and *Et* ester, m.p. 86°), thus prepared, are also synthesised by condensing *o*-OMe·C_6H_4·CHO with the appropriate COArMe in presence of 50% NaOH, giving *p*-anisyl, and 3 : 4-, 2 : 4-, m.p. 107°, and 2 : 5-, m.p. 77°, *-dimethoxyphenyl o-methoxystyryl ketones*, the respective *dibromides*, m.p. 89°, 170°, 171°, and 137°, of which are converted by KCN and hydrolysis into the above acids. *β-4-Methoxy-m-toluoyl-α-o-anisylpropionic acid*, m.p. 124° (*Et* ester, m.p. 105°), could not be so synthesised. *β-2-Hydroxy-4-methoxybenzoyl-α-o-anisylpropionic acid*, m.p. 165° (*Et* ester, m.p. 109°), is methylated (Me_2SO_4) to (**I**). All these CO-acids with *o*-OH·C_6H_4·CHO and piperonal give pyrylium and piperonylidene derivatives respectively. A. Li.

Friedel-Crafts reaction. VI. Further evidence for γ-substitution in resorcinol and orcinol derivatives. R. D. Desai and (Miss) V. M. Vakil (*Proc. Indian Acad. Sci.*, 1940, **12, A**, 391—398; cf. A., 1939, II, 23).—Conclusive evidence of simultaneous *β*- and *γ*-substitution or of *γ*-substitution alone has been obtained. AcCl, anhyd. orcinol (**I**), and $AlCl_3$ in $PhNO_2$ at room temp. and then at 100° gave only *γ*-orcacetophenone [2 : 6-dihydroxy-4-methylacetophenone] (**II**), m.p. 142—144°, in 20—25% yield in four out of seven attempts. In the other three experiments *β*-orcacetophenone (**III**) was also produced. (**II**) forms an *oxime*, m.p. 211—212°, and a p-*nitrophenylhydrazone*, m.p. 245°; it is reduced (Zn–Hg and boiling dil. HCl) to 5-*methyl*-2-*ethylresorcinol*, m.p. 135°. (**I**), BzCl, and $AlCl_3$ in $PhNO_2$ afford 2 : 4-dihydroxy-5-methylbenzophenone, m.p. 138°. Condensation of (**II**) or (**III**) with Ac_2O by $AlCl_3$ in $PhNO_2$ gives 2 : 4-*diacetyl*-5-*methylresorcinol*, m.p. 95° [p-*nitrophenylhydrazone* (mixture of *mono*- and *di*-), m.p. 242°]. Resacetophenone (**IV**), BzCl, and $AlCl_3$ in $PhNO_2$ afford 2-*benzoyl*-4-*acetylresorcinol* (**V**), m.p. 165° (p-*nitrophenylhydrazone*, m.p. >300°), which could not be brominated in $CHCl_3$ or AcOH at room temp. or condensed with Ac_2O in presence of $AlCl_3$, and 4-*O*-benzoylresacetophenone (**VI**) (Br_1-derivative, m.p. 176°), new m.p. 110°, hydrolysed to BzOH and (**IV**). (**VI**) is transformed by $AlCl_3$ at 140° into (**V**). 2 : 4 : 5 : 1-$(OH)_2C_6H_2Ac$·CO_2Me is converted by $AlCl_3$ and BzCl in $PhNO_2$ at room temp. and then at 130—140° into *Me* 2 : 4-*dihydroxy*-3-*benzoyl*-5-*acetylbenzoate*, m.p. 204°, hydrolysed by boiling 5% NaOH to (**V**) and the corresponding *acid*, m.p. 217°, which yields (**V**) when heated at 220—225°. 4 : 1 : 3-$C_6H_3Bz(OH)_2$ and Ac_2O in $PhNO_2$ containing $AlCl_3$ at 100° yield 4-*benzoyl*-2-*acetyl*- (**VII**), m.p. 107—108° (p-*nitrophenylhydrazone*, m.p. 227—229°), and 4-*benzoyl*-2 : 6-*diacetyl-resorcinol*, m.p. 151° [p-*nitrophenylhydrazone*, m.p. 288—290° (decomp.)]. (**VII**) is obtained synthetically from 2 : 1 : 3-$C_6H_3Ac(OH)_2$, $AlCl_3$, and BzCl in $PhNO_2$. H. W.

Reactivity of aryl *p*-alkoxystyryl ketones. R. P. Dodwadmath (*J. Univ. Bombay*, 1940, **9**, Part 3, 172—179).—2 : 4 : 1-$C_6H_3(OMe)_2$·COMe with 6-bromopiperonal (**I**) in boiling dil. aq. EtOH–NaOH gives two forms, m.p. 147—148° (yellow) and 137—138° (colourless) (the latter passing into the former when melted and resolidified), of 2 : 4-*dimethoxyphenyl* 6-*bromo*-3 : 4-*methylenedioxystyryl ketone* (**II**). Both forms give the same *phenylhydrazone*, m.p. 168—169°, with CH_2Ac·CO_2Et (NaOEt) give *Et* 5-2′ : 4′-*dimethoxyphenyl*-3-6′-*bromo*-3′ : 4′-*methylenedioxyphenyl*-Δ^5-cyclo*hexenone*-2-*carboxylate*, m.p. 152—153°, and with Br in $CHCl_3$–CCl_4 yield 5-*bromo*-2 : 4-*dimethoxyphenyl* *αβ-dibromo-β-6-bromo*-3 : 4-*methylenedioxyphenylethyl ketone*, m.p. 188—189°, converted by KI in $COMe_2$ into 5-*bromo*-2 : 4-*dimethoxyphenyl* 6-*bromo*-3 : 4-*methylenedioxystyryl ketone*, m.p. 257—258°, also obtained from 2 : 4 : 5 : 1-$(OMe)_2C_6H_2Br$·COMe and (**I**) as above. (**II**) with HI–Ac_2O yields 2-*hydroxy*-4-*methoxyphenyl* 6-*bromo*-3 : 4-*methylenedioxystyryl ketone* (**III**), m.p. 210—211° [also obtained from 2 : 4 : 1-OH·$C_6H_3(OMe)$·COMe and (**I**) as above], which with CH_2Ac·CO_2Et (NaOEt) gives *Et* 5-2′-*hydroxy*-4′-*methoxyphenyl*-3-6′-*bromo*-3′ : 4′-*methylenedioxyphenyl*-Δ^5-cyclo*hexenone*-2-*carboxylate*, m.p. 215—216°. The *acetate* (Ac_2O in C_5H_5N), m.p. 158—159°, of (**III**) with Br in $CHCl_3$–CCl_4 yields the *dibromide*, m.p. 194—195°, converted by aq. EtOH–NaOH at 80—90° into 5-*methoxy*-1-6′-*bromo*-3′ : 4′-*methylenedioxybenzylidenecoumaran*-2-*one*, m.p. 224—225°, and by KI in $COMe_2$ into (**III**). 2-Hydroxy-4-benzyloxyphenyl *p*-methoxystyryl ketone (**IV**) with Br in C_6H_6 yields the *dibromide*, m.p. 150—151°, converted by cold aq. EtOH–NaOH into 7-benzyloxy-4′-methoxyflavone [also obtained (Mahal *et al.*, A., 1935, 1129) by the action of SeO_2 on (**IV**)], and by further bromination in $CHCl_3$–CCl_4 into 5-*bromo*-2-

hydroxy-4-benzyloxyphenyl aβ-dibromo-β-p-anisylethyl ketone (V), m.p. 166—167°. KI in $COMe_2$ converts (V) into *5-bromo-2-hydroxy-4-benzyloxyphenyl p-methoxystyryl ketone* (VI), m.p. 153—154°, also obtained from 4 : 2 :1-$CH_2Ph{\cdot}O{\cdot}C_6H_3(OH){\cdot}COMe$ by bromination in CS_2 in presence of a trace of I, and condensation of the resulting *5-Br*-compound, m.p. 154—155°, with *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$ in boiling dil. aq. EtOH–NaOH. Oxidation (SeO_2 in $C_5H_{11}{\cdot}OH$ at 150°) of (VI) yields *6-bromo-7-benzyloxy-4′-methoxyflavone*, m.p. 200—201°, also obtained by the action of cold aq. NaOH or EtOH–KCN on (V) in $COMe_2$.



(VII.)

(V) with boiling aq. MeOH–Na_2CO_3 yields *4-bromo-5-benzyloxy-1-p-anisylidenecoumaran-2-one*, m.p. 209—210°. This adds Br in hot $CHCl_3$ giving the *dibromide*, m.p. 170—171° (loses Br when boiled with MeOH or EtOH), and with $CH_2Ac{\cdot}CO_2Et$ (NaOEt) gives the (?) *compound* (VII) (R = *p*-$OMe{\cdot}C_6H_4$·), m.p. 205—206°. A. LI.

4 : 5-Benz-Δ⁴-*cyclo*octenone. E. M. Fry and L. F. Fieser (*J. Amer. Chem. Soc.*, 1940, **62**, 3489—3494).—The Et_2 ester, b.p. 160—162°/2 mm., of *o*-$CO_2H{\cdot}CH_2{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}CO_2H$ (prep. in 67% yield from 2 : 3-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ by Na–*n*-$C_5H_{11}{\cdot}OH$ at 158—165°) with H_2–Cu chromite in dioxan at 185°/2400—2800 lb. gives 75% of *o-β-hydroxyethyl-γ-hydroxy-n-propylbenzene* (I), b.p. 174·5—175·5°/2 mm. Hydrogenation at 250° gives ≯40% of (I) and much $(OH)_1$-compound, $C_{11}H_{16}O$, b.p. 97—100°/2 mm. $SOCl_2$ at room temp. and later boiling converts (I) into the *dichloride*, b.p. 130—132°/2 mm., which with KCN in boiling aq. EtOH gives 63% of the *dinitrile*, b.p. 198° (196—212°)/2 mm. When this is run in Et_2O into boiling, stirred $C_{10}H_8$–Na–Et_2O–NHPhMe–N_2, it affords 71% of an isomeride-*A* (II), m.p. 146—147·5°, probably *2-cyano-4 : 5-benz-Δ⁴-cyclooctenoneimine*, and the impure isomeride-*B*, m.p. 124—126°, probably the 8-CN-derivative. Conc. HCl, first at room temp. and then warm, converts (II) into the *octenone* (III) (87%), m.p. 146—147·5° (sol. in N-NaOH), and hydrogenation (PtO_2) in Ac_2O gives *2-acetamidomethyl-4 : 5-benz-Δ⁴-cyclooctenone*, m.p. 153·5—154·5°. The crude imine-*B* similarly gives (with difficulty) *8-cyano-4 : 5-benz-Δ⁴-cyclooctenone*, m.p. 96·5—97·5°, and material of high m.p. With ~76·5 (vol.)% H_2SO_4 at 100° (5 min.) the respective cyanoketones give *4 : 5-benz-Δ⁴-cyclooctenone-2-* (82·5%), m.p. 130—131°, and *-8-carboxylamide* (96·5%), m.p. 239—241·5° (decomp.), but both give *4 : 5-benz-Δ⁴-cyclooctenone* (IV), m.p. 48·5—50·5° (*oxime*, m.p. 112·5—114°), when the diluted solution is heated at 100° for a further 15 min. Hydrogenation (PtO_2; EtOH) of the keto-amides gives *4 : 5-benz-Δ⁴-cyclooctenol-2-* (V), m.p. 181·5—182·5°, and *-8-carboxylamide*, m.p. 157·5—160°. With boiling 10% HI and a little red P or with 6N-HCl, (V) gives *4 : 5-benz-Δ⁴-cyclooctenol-2-carboxylic acid*, m.p. 132—134°, dehydrated by HI (*d* 1·7) and quinoline to *3 : 4-benz-Δ³:⁸-cyclooctadiene-1-carboxylic acid*, m.p. 140—140·5°. Hydrogenation (PtO_2; EtOH) then yields *3 : 4-benz-Δ³-cyclooctene-1-carboxylic acid* (VI), sinters at 77°, m.p. 78·5—80°. H_2–Cu chromite at 200°/2330 lb. reduces (IV) in dioxan to *4 : 5-benz-Δ⁴-cyclooctenol*, m.p. 63—65°, converted by PBr_3 in $CHCl_3$ at −8° to −5° into the bromide, b.p. 125—133°/2 mm., which affords (Grignard) *4 : 5-benz-Δ⁴-cyclooctene-1-carboxylic acid* (VII), sinters at 139°, m.p. 142—144°. Non-identity of (VI) and (VII) is the basis for orientation of the above-named isomerides. (IV) sublimes and is volatile in steam. With $MeNO_2$ in C_5H_5N at room temp. it gives a *compound*, $C_{14}H_{18}O_4N_2$, m.p. 106—107°. M.p. are corr. R. S. C.

Sulphur derivatives of β-diketones. I. Di-(2 : 6-diketo-4 : 4-dimethylcyclohexyl) sulphide. N. Kajola (*Suomen Kem.*, 1940, **13, B**, 20—21).—5 : 5-Dimethylcyclohexane-1 : 3-dione (I) (as Na, K, or Ag salt) and S in C_6H_6 or PhMe give *di-*(2 : 6-*diketo*-4 : 4-*dimethyl*cyclo*hexyl*) *sulphide* (II), m.p. 234—235° (slight decomp.), which gives a brown colour with EtOH–$FeCl_3$ and an insol. Ag_2 salt. (II) with alkaline H_2O_2 affords (I) and then $CMe_2(CH_2{\cdot}CO_2H)_2$. M. H. M. A.

Manufacture of bromobenzanthrones.—See B., 1941, II, 77.

Vat dyes of the benzanthrone series. XXIII. Synthesis of 8 : 8′-dimethoxyviolanthrone. T. Maki and A. Kikuchi (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 347—348B).—Mainly an account of work described previously (A., 1938, II, 499). A. T. P.

Benzoate, m.p. 163—164·5° (corr.), and acetate, m.p. 93—95° (corr.), of 3(α)-hydroxyætiocholan-17-one.—See A., 1941, III, 194.

Steroids and sex hormones. LXV. Preparation of Δ⁴-androstene-6 : 17-dione. L. Ruzicka, L. Grob, and S. Raschka (*Helv. Chim. Acta*, 1940, **23**, 1518—1529).—*trans*-Dehydroandrosterone benzoate, m.p. 249—251°, in $CHCl_3$ is converted by *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ in Et_2O–$CHCl_3$ at −4° and subsequently at room temp. into the 5 : 6-*oxide* (I), m.p. 218—220°, hydrolysed by dioxan–H_2O slowly at 100°, more rapidly at 130°, to *androstane-3 : 5 : 6-triol-17-one 3-benzoate* (II), m.p. 262—264° (decomp.). In a single instance *trans*-dehydroandrosterone acetate was oxidised by BzO_2H in $CHCl_3$ at −4° and then at room temp. to an *oxide* (III) (or mixture of stereoisomeric oxides) with const. m.p. 205—207°, $[\alpha]_D^{19}$ −28·2°±1° in $CHCl_3$, but repetition of the experiment or use of *o*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ yielded a uniform *oxide* (IV), m.p. 222—223°, $[\alpha]_D^{17}$ −12°±0·5° in $CHCl_3$. Dioxan–H_2O hydrolyses (III) at 100° and (IV) at 145—150° to *androstane-3 : 5 : 6-triol-17-one 3-acetate* (V), m.p. 231—232°, $[\alpha]_D^{19}$ +34·09°±1° in $CHCl_3$. (II) in $CHCl_3$ is oxidised by CrO_3 in glacial AcOH at room temp. to *androstane-3 : 5-diol-6 : 17-dione 3-benzoate* (VI), m.p. 256—257°, more conveniently obtained by similar oxidation of (I). Similarly (V) is oxidised to *androstane-3 : 5-diol-6 : 17-dione 3-acetate* (VII), m.p. 210—211°, more readily obtained from (IV). (VI) is hydrolysed by boiling N-KOH–MeOH and (VII) by boiling 5% K_2CO_3 in aq. MeOH to *androstane-3 : 5-diol-6 : 17-dione* (VIII), m.p. 297—298° (vac.; decomp.) [*dioxime*, m.p. 245—247° (decomp.)]. (VIII) is transformed by *p*-$C_6H_4Me{\cdot}SO_2Cl$ in abs. C_5H_5N at room temp. into the 3-*p*-toluenesulphonate, m.p. 133° (decomp.), slowly transformed by boiling C_5H_5N into *Δ³-androsten-5-ol-6 : 17-dione*, m.p. 238—240°, also prepared by sublimation of (VIII) with fuller's earth at 150°/high vac. It is hydrogenated (Pd–$CaCO_3$ in EtOH) to *androstan-5-ol-6 : 17-dione*, m.p. 225—228°, dehydrated by *p*-$C_6H_4Me{\cdot}SO_2Cl$ in boiling C_5H_5N to a *diketone*, $C_{19}H_{26}O_2$, m.p. 215—216°, $[\alpha]_D^{19}$ +21°±2° in $CHCl_3$, which does not contain a double linking aβ to CO. *Androstan-5-ol-6 : 17-dione 5-acetate*, m.p. 187°, passes at 200°/13 mm. into *Δ⁴-androstene-6 : 17-dione* (IX), m.p. 179—181°, $[\alpha]_D^{19}$ +96·8°±1° in $CHCl_3$. The androgenic action of (IX) is about two fifths of that of Δ⁴-androstene-3 : 17-dione; œstrogenic activity could not be detected. M.p. are corr. H. W.

Redox titrations of vat dye systems.—See B., 1941, II, 76.

[Composition and constitution of Turkey-red.] R. Haller (*Helv. Chim. Acta*, 1940, **23**, 1529).—A question of priority against Fierz-David *et al.* (A., 1941, II, 49). H. W.

1-*p*-Dimethylaminobenzeneazoanthraquinone, m.p. 243°.—See A., 1941, I, 128.

III.—TERPENES.

New optically active reagent for carbonyl compounds. Resolution of *dl*-camphor. R. B. Woodward, T. P. Kohman, and G. C. Harris (*J. Amer. Chem. Soc.*, 1941, **63**, 120—124).—*l-Menthyl N-aminocarbamate* [termed "*menthydrazide*"] (I), m.p. 101·5—102°, [*M*] −171°, condenses readily with CO-compounds and permits ready prep. of *l*- from *dl*-camphor. Its general use for resolution of ketones and aldehydes is proposed. Menthol, Me_2CO_3, and Na at 200° give MeOH and di-*l*-menthyl carbonate, m.p. 105—106°, [*M*] −308°, converted by boiling $ClCO_2Et$ and a little C_5H_5N into *l-menthyl Et carbonate*, m.p. 20·5°, b.p. 121°/9 mm., which with $N_2H_4{\cdot}H_2O$ in cellosolve yields (I). Formation of "menthydrazones" is generally best effected by a little NaOAc–AcOH in boiling EtOH, and hydrolysis by short boiling in 5—10% H_2SO_4. The following are described. *Acetone-*, m.p. 191—192°, [*M*] −163°, *Me Et ketone-*, m.p. 146—147°, [*M*] −156°, *acetophenone-*, m.p. 164—165°, [*M*] −187°, *benzylideneacetophenone-*, m.p. 169—170°, [*M*] −123°, *Et acetoacetate-*, m.p. 92—93°, [*M*] −160°, *Et lævulate*, m.p. 117—117·5°, [*M*] −186°, *benzaldehyde-*, m.p. 164—164·5°, [*M*] −182°, *cinnamaldehyde-*, m.p. 176—177°, [*M*] −161°, d-*glucose-*, m.p. 187—189°, [*M*] −226°, *d-*, m.p. 177—178°, [*M*] −236°, and l-*camphor-*, m.p. 193—194°, [*M*] −101°, *-l-menthydrazide*. [*M*] are $[M]_D^{25}$ in EtOH. R. S. C.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Reaction of methyl hypochlorite with lignin. E. E. Harris and L. J. Lofdahl (*J. Amer. Chem. Soc.*, 1941, **63**, 112—114).—When maple lignin is treated with MeOCl, addition of two mols. and chlorination occur; spruce lignin adds 2—3 mols. and undergoes chlorination. The results differ quantitatively, but not qualitatively, according to whether the MeOCl is presented as Cl_2–MeOH, Cl_2–$BaCO_3$–MeOH, $NCl_2{\cdot}CO{\cdot}NH_2$–MeOH, or MeOCl–$CCl_4$–MeOH. Temp. (5—30°) has only a minor effect. R. S. C.

Aromatic aldehydes from spruce and maple woods. R. H. J. Creighton, J. L. McCarthy, and H. Hibbert (*J. Amer. Chem. Soc.*, 1941, **63**, 312).—Prep. of vanillin (**I**) (22·8—24·7%) from spruce wood meal by 2*N*-NaOH and $PhNO_2$ at 160° (Freudenberg *et al.*, A., 1940, II, 352) is confirmed. 3·4% of (**I**) and 31·8% of syringaldehyde are similarly obtained from maple wood. % yields refer to the original Klason lignin content. R. S. C.

Chloro-derivatives of ligninsulphonic acids. A. V. Karateev (*J. Appl. Chem. Russ.*, 1940, **13**, 751—761).—Chlorination of ligninsulphonic acid yields H_2O-sol. and -insol. fractions, in which the former contain more Cl and S than the latter. One OMe is eliminated per 3·8 Cl introduced into the former, and per 2·6 Cl into the latter, fraction. Chlorination of sulphite lye also gives a sol. and an insol. fraction, but in this case the latter contains more Cl than the former. R. T.

V.—HETEROCYCLIC.

β-2-Furylethanol and β-2-furylethyl chloride. E. D. Amstutz and J. Plucker, tert. (*J. Amer. Chem. Soc.*, 1941, **63**, 206—207).—*β-2-Furylethyl alcohol* (prep. from Et 2-furylacetate by Na–EtOH at 145° in 32% yield), b.p. 86—88°/21 mm. (*α-naphthylurethane*, m.p. 85·2—86°), and $SOCl_2$–C_5H_5N–Et_2O give the *chloride*, b.p. 63°/26 mm., which by way of the derived Grignard reagent gives γ-2-furylpropionic acid. R. S. C.

Hydrogenation of hydrofuramide and furfuraldehyde.—See B., 1941, II, 37.

Condensation products of trimethylquinol and halides (tocopherols).—See B., 1941, III, 21.

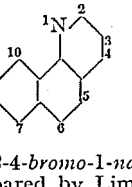
Heterocyclic compounds. XI. Application of the Pechmann and the Kostanecki reactions to γ-orcacetophenone. R. D. Desai and (Miss) V. M. Vakil (*Proc. Indian Acad. Sci.*, 1940, **12, A**, 357–360).—γ-Orcacetophenone [2 : 6 : 4 : 1-$(OH)_2C_6H_2Me{\cdot}COMe$] (**I**) condenses with $CH_2Ac{\cdot}CO_2Et$ in presence of conc. or 73% H_2SO_4 at room temp. or of $POCl_3$ in boiling C_6H_6 to 5-hydroxy-4 : 7-dimethylcoumarin, m.p. 256°. Prolonged treatment of (**I**) with NaOAc and Ac_2O at 175—180° affords *5-acetoxy-3-acetyl-2 : 7-dimethylchromone*, m.p. 103° [hydrolysed by conc. H_2SO_4 at room temp. to the 5-*OH*-compound (**II**), m.p. 141°, which is converted by boiling 5% NaOH into *p*-orsellinic acid (**III**)], (**II**), and 5-hydroxy-4-acetonyl-7-methylcoumarin identified by its alkaline hydrolysis to 5-hydroxy-4 : 7-dimethylcoumarin and (**III**). In these reactions (**I**) differs essentially from its isomeric β-orcacetophenone (A., 1939, II, 173). H. W.

Condensation of methyl phloroglucinolcarboxylate with ethyl acetoacetate. S. M. Sethna (*J. Univ. Bombay*, 1940, **9**, Part 3, 104—106).—2 : 4 : 6 : 1-$C_6H_2(OH)_3{\cdot}CO_2H$ could not be condensed with $CH_2Ac{\cdot}CO_2Et$, but its Me ester in presence of $AlCl_3$ in Et_2O or of 80% H_2SO_4 yields *Me 5 : 7-dihydroxy-4-methylcoumarin-6*(or 8)*-carboxylate*, m.p. 230—231° (*diacetate*, m.p. 161—162°; *Me₂ ether*, m.p. 182—183°), hydrolysed (NaOH) to 5 : 7-dihydroxy-4-methylcoumarin. A. Li.

Constitutional factors controlling visible fluorescence in compounds of the benzopyrone group. S. Rangaswami and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1940, **12, A**, 375—380).—Examination of many coumarins shows that the essential requirement for the production of fluorescence is the presence of OH at $C_{(7)}$. Fluorescence is developed in alkaline solution or in conc. H_2SO_4, being more marked in the former and obviously due to formation of ions. Its gradual disappearance in alkaline solution is due to the opening of the pyrone ring. Replacement of OH by OMe or $O{\cdot}C_3H_5$ at $C_{(7)}$ causes disappearance of fluorescence in alkaline but not in acid solution. 7-Acetoxycoumarin gradually develops fluorescence owing to hydrolysis. Alkyl at $C_{(4)}$ or $C_{(5)}$ enhances and at $C_{(8)}$ considerably reduces the fluorescence of 7-hydroxycoumarin. CHO, Ac, or NO_2 at $C_{(8)}$ completely inhibits, and Br abolishes or weakens, fluorescence. CO_2Et or CO_2H at $C_{(3)}$ greatly enhances fluorescence and causes it to become blue. If OH is not present at $C_{(7)}$ but at $C_{(8)}$ a yellow solution without fluorescence is produced. 5 : 7- and 7 : 8-Dihydroxycoumarin are non-fluorescent but the 6 : 7-compound gives a weak blue fluorescence. Coumaric acid is feebly fluorescent in alkaline solution but not in H_2SO_4 and the property is greatly intensified by the presence of traces of Hg. In presence of OH the loss of fluorescence is accelerated by the presence of Hg. In the flavone, *iso*flavone, and chromone series fluorescence is frequent in conc. H_2SO_4 but very rare in alkaline solutions, 7-hydroxy-3-methoxy-2-methylchromone and 7-hydroxy-2-methyl*iso*flavone alone exhibiting fluorescence under the last conditions. Further the fluorescence of flavones does not appear to depend on the presence of OH and the position of OH in the different rings appears to have no sp. influence. The only reasonable generalisation appears to be that all the simple OH-derivatives of chromones, flavones, and *iso*flavones are fluorescent. The presence of a large no. of OH has an adverse effect which is modified if some of them are methylated. In flavones transformation of OH at $C_{(7)}$ into OAc, OMe, or $O{\cdot}C_3H_5$ does not produce a marked change. Me at $C_{(8)}$ destroys the capacity to fluoresce whereas one or two $CH_2{:}CH{\cdot}CH_2$ *ortho* to OH modify the colour of the fluorescence to green. Ac at $C_{(3)}$ or $C_{(8)}$ inhibits fluorescence. The influence of substituents in chromones appears to be on the same lines but there are small differences particularly in intensity. H. W.

Piperidine and quinoline derivatives.—See B., 1941, II, 37.

Derivatives of benzo[*h*]quinoline [α-naphthoquinoline]. W. P. Utermohlen, jun., and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1941, **63**, 156—159).—4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$, syrupy H_3AsO_4, glycerol, conc. H_2SO_4, and AcOH at 120° give a poor yield of *6-nitro-α-naphthoquinoline*, m.p. 149°. 5 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$, $FeSO_4$, glycerol, H_3BO_3, H_3AsO_4, and H_2SO_4 at 140° give *7-nitro-α-naphthoquinoline*, m.p. 174·5—175°, in poor yield. No such product could be obtained from 8 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$. 4 : 1-$C_{10}H_6Br{\cdot}NH_2$, H_3AsO_4, glycerol, and H_2SO_4 at 95—125°, later 135°, give *6-bromo-α-naphthoquinoline*, m.p. 111·5—116°. 4-Hydroxy- and *6-bromo-4-hydroxy-*, m.p. >270°, *-2-methyl-α-naphthoquinoline* and *Et β-4-bromo-1-naphthylaminocrotonate*, m.p. 113—114°, are prepared by Limpach's method. 4-Chloro-2- (**I**) and 2-chloro-4-methyl-α-naphthoquinoline (**II**) are prepared in 50% yield from the corresponding OH-compounds by PCl_5 in $(CHCl_2)_2$. PCl_5–$POCl_3$ and the 4-OH-compound give 25% of *4-chloro-6-bromo-2-methyl-α-naphthoquinoline*, m.p. 146·5—147°. $Cl{\cdot}[CH_2]_2{\cdot}CN$ with $NHEt_2$ or morpholine gives (cooling) *β-diethylamino-*, b.p. 83·5—84·5°/13 mm., and *β-morpholino-propionitrile*, b.p. 133—134°/14 mm., respectively. $Cl{\cdot}[CH_2]_3{\cdot}CN$ gives (boiling) similarly *γ-diethylamino-*, b.p. 91—100°/14 mm., and *γ-morpholino-butyronitrile*, b.p. 142°/15 mm., reduced by Na–EtOH–PhMe to *δ-diethylamino-*, b.p. 85—86°/16 mm., and *δ-morpholino-butylamine*, b.p. 123—125°/15 mm., respectively. γ-Diethylamino- and *γ-morpholino-propylamine*, b.p. 103—105°/15 mm., are similarly prepared. Condensation of (**I**) or (**II**) with the appropriate base affords *2-morpholino-4-*, m.p. 101·5°, *4-morpholino-2-* (**III**), m.p. 127·5°, *2-β-hydroxyethylamino-4-*, m.p. 108°, *4-β-hydroxyethylamino-2-* (**IV**), m.p. 181—181·5°, *2-piperidino-4-*, m.p. 79—80°, *4-β-chloroethylamino-2-* [prep. from (**IV**) by $POCl_3$], m.p. (anhyd.) 153°, (+0·5MeOH) 83—84°, *2-ethylideneamino-4-* [prep. from (**III**) by $SOCl_2$], amorphous, m.p. 184·5—186·5° (decomp.), *4-γ-diethylamino-n-propylamino-2-*, m.p. 84—85°, *2-γ-diethylamino-n-propylamino-4-*, b.p. 275—280°/5 mm., *4-δ-diethylamino-n-butylamino-2-*, m.p. 98—100°, *2-δ-diethylamino-n-butylamino-4-*, b.p. 240—245°/2 mm., *4-δ-morpholino-n-butylamino-2-*, m.p. 110—112°, *2-δ-morpholino-n-butylamino-4-*, b.p. 285—290°/4 mm., and *2-γ-morpholino-n-propylamino-4-*, m.p. 83—84°, *-methyl-α-naphthoquinoline* and *α-morpholino-γ-di-2-methyl-4-α-naphthoquinolylaminopropane*, m.p. 151—152·5°. R. S. C.



Pyrimidines. CLXVI. Chlorination of pyrimidine thiocyanates. T. B. Johnson and G. de Sütö-Nagy (*J. Amer. Chem. Soc.*, 1941, **63**, 261—263; cf. A., 1940, II, 382).—2-Chloro-5-thiocyanopyrimidine, m.p. 125—126°, does not react with Cl_2 in AcOH or 60% MeOH at room temp. or H_2O at

70°. In aq. EtOH at 15—25° the pyrimidine ring is ruptured, but *substances*, $C_4H_3O_2N_2Cl_3$, possibly 2 : 5 : 5-trichloro-4 : 6-dihydroxy-5 : 6-dihydropyrimidine, m.p. 228—229° [in boiling H_2O gives a substance, m.p. 295—300° (decomp.)], and $C_3H_3ON_2Cl$, possibly 2-chloro-4-hydroxyglyoxaline, m.p. >300°, and 5-chlorouracil are isolated. R. S. C.

Pyrimidines. CLXVII. Dehydrogenation of hydrouracil. T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 263—264).—Hydrouracil is unaffected by H_2O_2 or dichlorohydroxymethylhydrouracil but is smoothly oxidised by alloxan (**I**) in boiling H_2O to uracil (5-*NO*$_2$-derivative, m.p. 280—285°), the (**I**) yielding $H_2C_2O_4$ and $CO(NH_2)_2$. R. S. C.

N^1N^4-Pyrazinoyl derivatives of sulphanilamide. T. C. Daniels and H. Iwamoto (*J. Amer. Chem. Soc.*, 1941, **63**, 257—258).—Pyrazinoyl chloride (**I**) (prep. by PCl_3–PCl_5 or by PCl_5–C_6H_6 at 80—85°) with *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ in boiling C_5H_5N gives N^4-*pyrazinoyl-* (**II**), m.p. 247—248° (N^1-*Ac* derivative, m.p. 249—250°), and with *p*-NHAc·$C_6H_4{\cdot}SO_2{\cdot}NH_2$ in boiling C_5H_5N gives N^1-*pyrazinoyl*-N^4-*acetyl-sulphanilamide* (**III**), m.p. 262—264°. In boiling C_5H_5N, (**I**) and (**II**) give N^1N^4-*dipyrazinoyl-*, m.p. 286—290°, and hydrolysis of (**III**) by boiling 10% NaOH gives N^1-*pyrazinoyl-sulphanilamide*, m.p. 246—248° [depresses the m.p. of (**II**)]. M.p. are corr. R. S. C.

4-β-Piperidylethylquinoline.—See B., 1941, I, 17.

Porphyrins. IV. Synthesis of αβγδ-tetraphenylporphins. P. Rothemund and A. R. Menotti (*J. Amer. Chem. Soc.*, 1941, **63**, 267—270).—Synthesis of the two αβγδ-tetraphenylporphins, acid no. 13·5 and 8·5 (A., 1940, II, 27), from pyrrole, PhCHO, and C_5H_5N in boiling MeOH (at 220° without MeOH only the former is obtained) and the absorption of the former and of its hydrochloride are detailed. Isomerism depends on the position of the ethylenic linkings in the mol. R. S. C.

Phthalocyanines.—See B., 1941, II, 77.

Catalytic dehydration of β-morpholinoethanol. H. W. Block with J. P. Mason (*J. Amer. Chem. Soc.*, 1941, **63**, 298—300).—When passed over activated Al_2O_3 at 270—300°, β-morpholinoethyl alcohol gives morpholine (12%), αβ-dimorpholinoethane (6%), di-β-morpholinoethyl ether (6%), and C_2H_2, probably by decomp. of 4-vinylmorpholine. β-Morpholinoethyl chloride and KOH–EtOH give the Et ether. R. S. C.

2 : 6-Dimethylmorpholinoethanol.—See B., 1941, II, 38.

αβ-Unsaturated ketones. III. α- and β-Morpholinobenzylideneacetone. N. H. Cromwell (*J. Amer. Chem. Soc.*, 1940, **62**, 3470—3473).—CHPhBr·CHBr·COMe with NaOAc in boiling EtOH gives CHPh:CBr·COMe (**I**), b.p. 119—121°/1 mm., and with morpholine (**II**) in abs. EtOH at room temp. gives exothermally βγ-*dimorpholino-γ-phenylbutan-β-one* (**III**), m.p. 159—160°, and small amounts of β-*morpholino-α-phenyl-*Δ^{α}-*buten-γ-one* (**IV**), m.p. 74—76°. Hydrolysis of (**III**) by boiling 10% H_2SO_4 gives PhCHO, $CH_2Ph{\cdot}CO{\cdot}COMe$ (**V**), and small amounts of acids; that of (**IV**) gives (**V**). In Et_2O–light petroleum, (**II**) and (**I**) give β-*bromo-β-morpholino-α-phenylbutan-γ-one* (**VI**), m.p. 100—101° (decomp.; instantaneous), which with NaOEt–EtOH gives (**IV**). Addition of (**II**) to (**IV**) is not feasible. Interaction of (**II**) and (**VI**) gives (**III**) and a little (**IV**). $COMe{\cdot}CH_2Bz$, (**II**), and a drop of conc. HCl, first boiling and then at room temp., give γ-*morpholino-α-phenyl-*Δβ-*buten-α-one*, m.p. 144—146°, hydrolysed by 10% HCl at 50° to $COMe{\cdot}CH_2Bz$. MgPhBr and (**III**) in C_6H_6–Et_2O give αβ-*dimorpholino-αγ-diphenylbutan-γ-ol*, m.p. 201—202°, which is also obtained from αβ-dimorpholino-αγ-diphenylpropan-γ-one by MgMeI, resists hydrolysis by acid or alkali, and, when oxidised, gives COPhMe as sole identifiable product. R. S. C.

Dimorphism of sulphathiazole. D. C. Grove and G. L. Keenan (*J. Amer. Chem. Soc.*, 1941, **63**, 97—99).—2-Sulphanilamidothiazole exists in forms, m.p. 200—202° and 173—175°, respectively, for which methods of prep., photomicrographs, and optical data are given. R. S. C.

Polymerisation of dyes in solution. Thionine and methylene-blue.—See A., 1941, I, 98.

Further synthesis of *N'*-substituted heterocyclic derivatives of sulphanilamide. K. Ganapati (*Current Sci.*, 1940, **9**, 457—458).—A preliminary note describing 7-sulphanilamidoalloxazine, 5-sulphanilamidobarbituric acid, 4-sulphanilamidouracil; 2-sulphanilamido-pyrimidine, -4-methylpyrimidine, and -2 : 4-dimethylpyrimidine; 2-sulphanilamido-1 : 3 : 4-thiodiazole, m.p. 216—218°, and -5-methyl-1 : 3 : 4-thiodiazole, m.p. 180—182°. Sulphanilamido-derivatives were also prepared from adenine and 4 : 5-diaminouracil. F. R. G.

Effect of ultra-violet radiation on nicotine. C. H. Rayburn, W. R. Harlan, and H. R. Hanmer (*J. Amer. Chem. Soc.*, 1941, **63**, 115—116).—Irradiation (2250—3050 A.) of nicotine at 60—65° gives oxynicotine [picrate, m.p. 169° (lit. 154—155°], nicotinic acid, and NH_2Me. R. S. C.

South African *Senecio* alkaloids. H. L. de Waal (*Nature*, 1940, **146**, 777—778).—Isatidine (**I**), and a new *alkaloid*, possibly $C_{18}H_{25}O_5N$, have been isolated from *S. retrorsus*. Catalytic hydrogenation of (**I**) (4 H_2) gives cryst. hexahydrodeoxyisatidine, $C_{18}H_{31}O_6N$. Hydrolysis [$Ba(OH)_2$] gives isatinecic acid and isatinecine. *Rosmarinine*, $C_{18}H_{27}O_6$, has been isolated from *S. rosmarinifolius*, Linn., and is hydrolysed to *rosmarinecine*, $C_8H_{15}O_3N$, and senecic acid. *S. pterophorus*, D.C., contains *pterophine* (**II**), $C_{18}H_{23}O_5N$, which can be hydrolysed to retronecine and pterophnecic lactone. *S. ilicifolius*, Thunb., contains senecionine, (**II**), and retrorsine. L. S. T.

Structure of monocrotaline. V. Retronecine, a derivative of 1-methylpyrrolizidine. R. Adams and E. F. Rogers (*J. Amer. Chem. Soc.*, 1941, **63**, 228—236; cf. A., 1940, II, 378).—Heliotridane (**I**) is shown to be 1-methylpyrrolizidine by synthesis of 1 : 3-*dimethyl*-2-n-*propylpyrrolidine* (**II**) (of which stereoisomeric forms are isolated), identical with *dl*-dihydrode-*N*-methylheliotridane (**III**). Menshikov's arguments (A., 1938, II, 162) are, however, inconclusive. $CN{\cdot}CHMe{\cdot}CO_2Et$, $OPh{\cdot}[CH_2]_2{\cdot}Br$, and K_2CO_3 at 145°/100 mm. (reflux) give *Et α-cyano-γ-phenoxy-α-methyl-*n-*butyrate*, b.p. 180—181°/2 mm., hydrolysed by KOH–aq. EtOH to the *acid*, m.p. 109—110°, which at 185° gives CO_2 and γ-*phenoxy-α-methyl-*n-*butyronitrile* (**IV**), b.p. 165—170°/19 mm., a *substance*, $C_{18}H_{24}O_3N_2$, m.p. 91—92°, and a little (**IX**) (see below). $MgPr^{\alpha}Br$ and (**IV**) in Et_2O at room temp. give *α-phenoxy-γ-methyl-*n-*heptan-δ-one* (**V**), b.p. 168—170°/19 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 85—87°), converted by H_2–PtO_2 in NH_2Me–MeOH at 70° into δ-*methylamino-α-phenoxy-γ-methyl-*n-*heptane* (**VI**), b.p. 175—176°/20 mm. (*picrate*, m.p. 115—116°), which with boiling 48% HBr gives 89% of (**II**) [= *dl*-(**III**)], b.p. 163—165° [*picrate, form* (**VII**), m.p. 115—116°; *picrolonate*, m.p. 162—163°; *methiodide*, m.p. 159—160°]. NH_2Me and (**V**) at 140° give δ-*methylimino-α-phenoxy-γ-methyl-*n-*heptane*, b.p. 173—175°/19 mm., which with HBr gives (**II**) [picrate (**VII**)], but with H_2–Raney Ni in dioxan at 140° gives only a little (**II**). H_2–NH_2Me–Cu chromite at 140° converts (**V**) into (**VI**) and (**II**) (*picrate, form*, m.p. 125—126°). Dehydrogenation of (**II**) by 40% Pd-asbestos at 280° gives the pyrrole, reduced by H_2–Cu chromite at 220° to (**II**), which, however, gives a *methiodide*, m.p. 178—179°. Prep. of heliotridene, b.p. 165—167°, $[\alpha]_D^{24}$ (freshly prepared) +38·89°, (after 10 days) +30·84°, (after boiling with NaOEt–EtOH) +27·46° (cf. lit.), (**I**), and thence of *d*-(**III**), $[\alpha]_D^{24}$ +6·92° (picrate, m.p. 125—126°; methiodide, m.p. 134—135°), are described. Dehydrogenation and subsequent hydrogenation of *d-* gives *dl*-(**III**). $CMeNa(CO_2Et)_2$ and $Cl{\cdot}[CH_2]_2{\cdot}Br$ in PhMe give *Et*$_2$ *β′-chloroethylmethylmalonate*, b.p. 144—145°/20 mm., which with boiling aq. NaOH gives the OH-ester, converted by boiling aq. H_2SO_4 into *α-methylbutyrolactone* (92%), b.p. 200—201°/745 mm. With NH_2Me at 280° this gives 1 : 3-*dimethyl-2-pyrrolidone* (94%), b.p. 105—110°/30 mm., converted by $MgPr^{\alpha}Br$ in C_6H_6 (not Et_2O) into 1 : 3-*dimethyl-2* : 2-*di-*n-*propylpyrrolidine*, b.p. 112—113°/30 mm. $CMeNa(CO_2Et)_2$ and $OPh{\cdot}[CH_2]_2{\cdot}Br$ in boiling PhMe give *Et*$_2$ *β-phenoxyethylmethylmalonate*, b.p. 180—185°/2 mm., and thence $OPh{\cdot}[CH_2]_2{\cdot}CHMe{\cdot}CO_2H$, m.p. 80°. The derived *amide*, m.p. 97—98°, with $MgPr^{\alpha}Br$ in boiling C_6H_6 gives 15% of (**V**). Retronecanol and $SOCl_2$ at 0° give *chlororetronecane* (38%), b.p. 112°/32 mm., $[\alpha]_D^{30}$ +53·79°, hydrogenated (Raney Ni; EtOH; 2—3 atm.) to (**I**), b.p. 165—166°, $[\alpha]_D^{23}$ −92·06° (picrate, m.p. 236°). M.p. are corr. R. S. C.

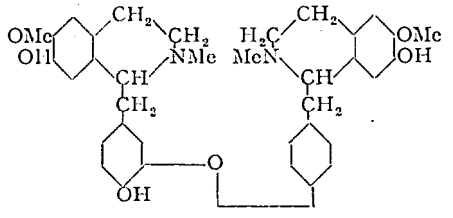
Alkaloids of fumariaceous plants. XXX. Aurotensine. R. H. F. Manske (*Canad. J. Res.*, 1940, **18, B**, 414—417).—Ethylation ($CHMeN_2$) followed by oxidation ($KMnO_4$) of aurotensine (**I**) (A., 1940, II, 238) gives 6-methoxy-7-ethoxy-1-keto-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (**II**) and 4-methoxy-3-ethoxyphthalic acid, both obtained similarly from scoulerine. It is concluded that (**I**) is an additive compound of *l-* and *dl-*scoulerine. Oxidation ($KMnO_4$) of cory-, m.p. 120° (corr.),

and *iso*cory-palmine Et ester, m.p. 82° (corr.) (not sharp), yields 7-methoxy-6-ethoxy-1-keto-1 : 2 : 3 : 4-tetrahydro*iso*quinoline and (**II**) respectively. A. Li.

Preparation of *N*-allylmorphine. E. L. McCawley, E. R. Hart, and D. F. Marsh (*J. Amer. Chem. Soc.*, 1941, **63**, 314).—Normorphine and CH_2:$CH{\cdot}CH_2Br$ at 70° give *N-allylmorphine*, m.p. 92—93° (*hydrobromide*, m.p. 126°), which antagonises morphine more strongly than does *N*-allylcodeine. R. S. C.

Alkaloids of *Aconitum* species. I. *A. thalassicum*. R. A. Konovalova and A. P. Orekhov (*J. Gen. Chem. Russ.*, 1940, **10**, 745—755).—The following alkaloids are isolated from this species: *thalatisine* (**I**), $C_{19}H_{23}(NMe)(OH)_3$, m.p. 246—246·5° [*hydrochloride*, m.p. 256—257°; *picrate*, m.p. 247—250° (decomp.); *perchlorate*, m.p. 222° (decomp.); *hydriodide*, m.p. 265° (decomp.); *triacetate*, m.p. 213—214° (*perchlorate*, m.p. 165—166°; *methiodide*, m.p. 253—254°, with decomp.); H_2-derivative, m.p. 262—263° (*picrate*, m.p. 230—231°; *hydrochloride*)]. With SO_2Cl_2 (**I**) affords the *trichloride* of (**I**), $C_{19}H_{23}Cl_3NMe$, m.p. 175—176°. Other alkaloids are: *thalatisamine*, $C_{19}H_{24}(NH)(OH)(OMe)_3$, m.p. 137—141° (*hydrochloride*, m.p. 186—189°); *thalatisidine*, $C_{19}H_{23}(NEt)(OH)_3(OMe)_2$, m.p. 220—221° [*perchlorate*, m.p. 218—220°; *hydrochloride*, m.p. 186—189°; *picrate*, m.p. 161—164° (decomp.)], and its isomeride, iso*thalatisidine*, m.p. 139—140°. R. T.

Alkaloids of *Magnolia fuscata*. II. Structure of magnoline. N. F. Proskurnina and A. P. Orekhov (*J. Gen. Chem. Russ.*, 1940, **10**, 707—713; cf. A., 1938, II, 515).—Magnoline (**I**) and CH_2N_2 or $CHMeN_2$ yield *trimethyl-*, m.p. 109—110°, or *triethyl-magnoline*, oxidised ($KMnO_4$ in $COMe_2$) to 4-(2′-methoxy- or 4-(2′-ethoxy-5′-carboxyphenoxy)benzoic acid and 1-keto-6 : 7-dimethoxy- or 1-keto-6-methoxy-7-ethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline. The structure of (**I**) is therefore



R. T.

VI.—ORGANO-METALLIC COMPOUNDS.

Stereochemistry of tervalent arsenic. III. Preparation of *p*-ethylphenylarsinobenzoic acid, and its attempted resolution into optical antipodes. G. Kamai (*J. Gen. Chem. Russ.*, 1940, **10**, 733—735).—PhAsO is converted into *phenylethyliodoarsine*, AsPhEtI, b.p. 139—140°/8 mm., which with *p*-$C_6H_4Me{\cdot}MgBr$ gives *p*-$C_6H_4Me{\cdot}AsPhEt$, oxidised by aq. $KMnO_4$ to p-*carboxydiphenylethylarsine oxide* [*hydrochloride*, m.p. 154—155° (decomp.)]. This is converted into p-*carboxydiphenylethylarsine*, m.p. 124—125°, the *strychnine*, m.p. 204—205°, and *quinine* salt, m.p. 182—183°, of which could not be resolved. *Phenyl*-m-*tolylethylarsine*, b.p. 174—174·5°/10 mm., similarly prepared, did not yield identifiable products when oxidised with $KMnO_4$. R. T.

Preparation of phenylarsinoxides. IV. Disubstituted compounds. G. O. Doak, H. G. Steinman, and H. Eagle (*J. Amer. Chem. Soc.*, 1941, **63**, 99—101; cf. A., 1940, II, 111).—Reduction of the appropriate arsinic acid by SO_2 gives 2 : 6-*dimethyl-*, 3-*nitro*-4-*methoxy-* and *-carboxy-*, 3-*chloro*-4-*hydroxy-*, 3 : 4-*diacetamido-*, 5- and 3-*amino*-2-*hydroxy-*, 5-*amino*-3-*hydroxy-*, 3 : 4-*dihydroxy-*, 3-*amino*-4-*carboxy-* (*amide*), -chloro-, and -*β-hydroxyethyl-phenylarsinoxide*. The Bart reaction affords 2 : 6-*dimethylphenylarsinic acid*, m.p. 207—208° (corr.). 3-*Nitro*-4-*β-hydroxyethyl-* (by nitration of the 4-*β*-acetoxyethyl-acid), m.p. 119—120° (corr.), 4-*chloro*-3-*amino-*, and 3-nitro-4-sulpho- (*Na*$_2$ salt) -*phenylarsinic acid*, 3 : 4-diamino- (*dihydrochloride*), 3 : 4-*dihydroxy-*, 4- [*hydrochloride*, m.p. 144—145° (corr.)], and 2-amino-3-hydroxy-phenyldichloroarsine [*hydrochloride*, m.p. 136—137° (corr.)], 3-nitro-4-sulpho- (*Na* salt), 4-*chloro*-3-*nitro-*, 3 : 4-dicarbomethoxy- and thence 3 : 4-*dicarboxylamido-phenylarsinous acid*, and *benziminazole*-6-*arsinous acid* are also prepared. R. S. C.

Reactions of 5-chloromercuri-2-furfuryl alcohol. W. J. Chute, W. M. Orchard, and G. F. Wright (*J. Org. Chem.*, 1941, **6**, 157—168).—Addition of a three-fold excess of furfuryl alcohol (**I**) to an aq. solution of $HgCl_2$ and NaOAc at room temp. gives a 50% yield of *5-chloromercuri-2-furfuryl alcohol* (**II**), m.p. 144·5—145·5°. If an equiv. amount of (**I**) is used the product contains more than simple substitution products since it is incompletely sol. in dil. alkali. With 5% NaOH (**II**) affords the *hydroxymercuri*-compound, m.p. 155—157°, which could not be freed from Na and Cl but is transformed by NaCl and CO_2 into (**II**). *5-Chloromercuri-2-furfuryl acetate* (**III**), m.p. 131—131·5°, is best obtained in 97% yield by acting on (**II**) in anhyd. C_5H_5N with Ac_2O at 0° for 4 days and subsequently adding sufficient 1% HCl to neutralise the C_5H_5N; in poor yield it results from (**II**) and keten in $COMe_2$. *Hg di-5-hydroxymethyl-2-furyl* (**IV**), m.p. 147·5—148·5°, is obtained in 62% yield from (**II**) and $Na_2S_2O_3$ in H_2O or in 61% yield from (**II**) and an excess of CH_2N_2 in MeOH. (**IV**) and $HgBr_2$ in boiling EtOH give *5-bromomercuri-2-furfuryl alcohol*, m.p. 139—140° (yield 84%), also obtained (yield 70·8%) from (**II**) and NaBr in aq. EtOH. It is transformed by Br in $CHCl_3$ at 0° into *5-bromofurfuryl acetate*, b.p. 106—107°/13 mm. This is hydrolysed (KOH in aq. MeOH at room temp.) to *5-bromofurfuryl alcohol* (**V**), m.p. 43—44°, also prepared from 5-bromofurfuraldchyde by the Cannizzaro reaction. (**V**) is very unstable, becoming green after a short time and then rapidly giving a green tar. Quinol or $CO(NH_2)_2$ lowers the m.p. without stabilising the compound. It is more stable in solution and survives a period of 5 hr. in boiling C_6H_6 containing NaOAc. The conversion of 2-chloromercurifuran by keten into 2-furyl Me ketone (2 : 4-*dinitrophenylhydrazone*, m.p. 223°) is best effected in CCl_4 or $CHCl_3$. *5-Acetofuryl acetate*, m.p. 46·5—47° (*semicarbazone*, m.p. 173—174°), is obtained in poor yield by the action of keten on (**III**) in $CHCl_3$ at 64°. It is oxidised by alkaline $KMnO_4$ to dehydromucic acid and hydrolysed (KOH–aq. MeOH at room temp.) to *5-acetofurfuryl alcohol*, m.p. 43—44°, which affords CHI_3 when treated with I in alkaline solution. Gradual addition of solid $KMnO_4$ to (**IV**) in $COMe_2$ gives *Hg di-5-formyl-2-furyl* (**VI**), m.p. 262—263°, which appears to give an oxime, m.p. 114—116°. *5-Chloromercurifurfuraldehyde*, m.p. 218—219°, is obtained in 5% yield by oxidation of (**II**) with one equiv. of $KMnO_4$ and in 66% yield from equiv. amounts of (**VI**) and $HgCl_2$ in boiling EtOH. It is converted by Br in cold $CHCl_3$ into 5-bromofurfuraldehyde, m.p. 82°, and by I in dioxan into *5-iodofurfuraldehyde*, m.p. 127·5°, oxidised to 5-iodofuroic acid, m.p. 197—198°. H. W.

Metallation and halogen-metal interconversion reactions of halogenated phenyl ethers. W. Langham, R. Q. Brewster, and H. Gilman (*J. Amer. Chem. Soc.*, 1941, **63**, 545—549).—Under mild conditions *o-*, *m-*, or *p*-$C_6H_4I{\cdot}OPh$ or -$C_6H_4Br{\cdot}OPh$ and $LiBu^a$ or LiPh undergo interconversion ($RHal + LiR' \rightarrow LiR + R'Hal$); under drastic conditions the *p-*, but not the *o-* or *m-*, compounds undergo metallation, giving 2 : 4 : 1-$Li{\cdot}C_6H_3Hal{\cdot}OPh$, with $LiBu^a$, LiPh, or LiMe. Interconversion occurs more readily with $C_6H_4I{\cdot}OPh$ than with $C_6H_4Br{\cdot}OPh$ and not at all with $C_6H_4Cl{\cdot}OPh$; under drastic conditions *p*-$C_6H_4Br{\cdot}OPh$ (**I**) gives first *p*-$Li{\cdot}C_6H_4{\cdot}OPh$ and then 2 : 4 : 1-$Li{\cdot}C_6H_3Br{\cdot}OPh$, but *p*-$C_6H_4Cl{\cdot}OPh$ gives only and directly 2 : 4 : 1-$Li{\cdot}C_6H_3Cl{\cdot}OPh$. After long interaction of *o*-$C_6H_4Br{\cdot}OMe$ or *o-* or *p*-$C_6H_4I{\cdot}OMe$ with LiMe, interconversion and subsequent coupling gives good yields of $C_6H_4Me{\cdot}OMe$, but there is no interconversion with *p*-$C_6H_4Cl{\cdot}OMe$. In some cases, *e.g.*, *p*-$C_6H_4Cl{\cdot}OPh$, coupling probably occurs without interconversion. The nature of R in LiR is also of importance in determining the course of the reaction. More metallation of *p*-$C_6H_4Hal{\cdot}OPh$ is produced by LiPh than by $LiBu^a$. LiMe causes 14—20% of direct metallation of *p*-$C_6H_4Cl{\cdot}OPh$, (**I**), or *p*-$C_6H_4Hal{\cdot}OMe$. Under mild conditions the relative ease of interconversion with (**I**) is $LiPr^a > LiBu^a > LiPh$. Under forced conditions, LiMe undergoes some interconversion with *o*-$C_6H_4Br{\cdot}OMe$, *o-* or *p*-$C_6H_4I{\cdot}OMe$, or *o*-$C_6H_4I{\cdot}OPh$. R. S. C.

Unsymmetrical organo-bismuth compounds. H. Gilman and H. L. Yablunky (*J. Amer. Chem. Soc.*, 1941, **63**, 207—211).—Reactions, (*A*) $BiAr_2Hal + MgAr'Hal \rightarrow BiAr_2Ar' + MgHal_2$, and (*B*) $2MgArHal + BiAr'Hal_2 \rightarrow BiAr_2Ar' + 2MgHal_2$, are realised except when steric hindrance interferes; solutions must be freshly prepared. $BiAr_2Ar'$ are usually purified as dichloride, whence they are regenerated by N_2H_4. $BiAr_2Ar'$ are stable when pure, even in the solid state. The

following are prepared, the method being indicated in parentheses. *Bi o-tolyl dibromide* [from $Bi(C_6H_4Me\text{-}p)_3$ (I) (1) and $BiBr_3$ (0·5 mol.); 18% yield], m.p. 181°. Bi di-*p*-tolyl chloride [from (I) (1) and $BiCl_3$ (0·5 mol.)] and *iodide*, m.p. 147—148°. $\alpha\text{-}C_{10}H_7\cdot Bi(C_6H_4Me\text{-}p)_2$ (*A*; *B*), m.p. 129—130° (*dichloride*, m.p. 147°; *dibromide*, m.p. varies, ~126—127°). $\alpha\text{-}C_{10}H_7\cdot BiBr_2$ [from $BiAr_3$ (1 mol.) and $BiBr_3$ (1·8 mols.) in Et_2O–$CHCl_3$ or $-C_6H_6$]. $(p\text{-}C_6H_4Me)_2Bi\cdot C_6H_4Cl\text{-}p$ (*A*), m.p. 96—97°. $(o\text{-}C_6H_4Me)_2Bi\cdot C_{10}H_7\text{-}\alpha$ (*B*), m.p. 112—114° (*dichloride*, m.p. 140°; *dibromide*, m.p. 122°). *Bi di-p-chlorophenyl chloride*, m.p. 158—160°, and iodide, m.p. 139—140°. $(p\text{-}C_6H_4Cl)_2Bi\cdot C_{10}H_7\text{-}\alpha$ (*A*; *B*), m.p. 138—139° (*dichloride*, m.p. 132°; *dibromide*, m.p. 102—103°). $(p\text{-}C_6H_4Cl)_2Bi\cdot C_6H_4Me\text{-}o$ (*B*), m.p. 104—104·5° (*dichloride*, m.p. 132—133°; *dibromide*, m.p. 109—110°). $BiPh_2Cl$ (from $BiPh_3$ and $BiCl_3$ in Et_2O). $BiPh_2\cdot C_{10}H_7\text{-}\alpha$ (*A*), m.p. 114—115°. $BiPh_2\cdot C_6H_4Cl\text{-}p$ (*A*), m.p. 83—83·5°. $BiPh_2\cdot C_6H_4Me\text{-}p$, an oil (*dichloride*, m.p. 109—110°). $(p\text{-}OMe\cdot C_6H_4)_2Bi\cdot C_{10}H_7\text{-}\alpha$ (*B*), m.p. 135—136°. $(p\text{-}OEt\cdot C_6H_4)_2Bi\cdot C_{10}H_7\text{-}\alpha$ (*B*), m.p. 131—132°. $(2:4:6\text{-}C_6H_2Me_3)_2Bi\cdot C_{10}H_7\text{-}\alpha$ (*B*), m.p. 151—151·5°. *Bi tri-p-cymyl*, m.p. 87° (*dichloride*, m.p. 163—164°; *dibromide*, m.p. 101—103°), *-mesityl*, m.p. 134—135° (unstable dibromide, m.p. 91—93°; chlorinated dichloride, m.p. 149—150°), *-p-fluorophenyl*, m.p. 93—94°, and *-o-chlorophenyl*, m.p. 141°. $Li\cdot C_6H_4\cdot NMe_2\text{-}p$ and $BiCl_3$ in Et_2O give *Bi tri-p-dimethylaminophenyl*, m.p. 230° after darkening, which is unstable in solution, being decomposed by HCl, AcOH–$CHCl_3$–light petroleum, or Cl_2–$CHCl_3$ at 0°. R. S. C.

Reactions of organo-bismuth compounds in liquid ammonia. H. Gilman and H. L. Yablunky (*J. Amer. Chem. Soc.*, 1941, **63**, 212—216).—$BiAr_2Br$ and metals in liquid NH_3 give $BiAr_3M$ (M = Li, Na, or K) or $(BiAr_2)_2M$ (M = Ca or Ba), which decompose when kept but with $1\text{-}C_{10}H_7I$ afford $BiAr_2\cdot C_{10}H_7\text{-}\alpha$ (and varying amounts of $C_{10}H_8$). $BiPh_2\cdot C_{10}H_7\text{-}\beta$, similarly prepared, is an oil, giving an oily dichloride and thence a *dibenzoate*, m.p. 138—140°. $BiPh_2Na$ yields $p\text{-}C_6H_4Ph\cdot BiPh_2(OBz)_2$ and $BiPh_2\cdot C_6H_4\cdot NMe_2\text{-}p$, m.p. 187°, but in many cases $BiPh_3$ is obtained. Existence of $BiPh_2$ is evidenced by a transient green colour. $\alpha\text{-}C_{10}H_7\cdot BiBr_2$ and Na (4 atoms) give $\alpha\text{-}C_{10}H_7\cdot BiNa_2$, but subsequent addition of PhI gives only $C_{10}H_8$ and recovered PhI. Na–Bi does not react with PhI in liquid NH_3. Treatment of $BiPh_3$ in Et_2O–liquid NH_3 with Na and then $1\text{-}C_{10}H_7I$ gives 18·2% of regenerated $BiPh_3$ and 77·2% of $C_{10}H_8$, indicating unusual reactivity of the Na; $BiPh_3Cl_2$ behaves similarly, but $1\text{-}C_{10}H_7I$ and Na alone in NH_3 give only 47·2% of $C_{10}H_8$. $BiPh_2Li$ and $p\text{-}C_6H_4Br\cdot OH$ in Et_2O–NH_3 give $BiPh_3$ and a small amount of a product, $BiC_{18}H_{15}O$, m.p. 179—180° after sintering. *o-* and *p-* (not *m-*)$C_6H_4Hal\cdot CO_2H$ give unstable, H_2O-sol. compounds. The order of relative reactivity, $BiAr_2Cl > BiAr_2Br > BiAr_2I$, is observed. R. S. C.

Organo-silicon synthesis. III. Two-stage Wurtz reactions with silicon halides. W. C. Schumb and C. M. Saffer (*J. Amer. Chem. Soc.*, 1941, **63**, 93—95; cf. A., 1938, II, 476).—In the Wurtz type synthesis of $(SiR_3)_2$ or $(SiR_3)_2O$ from the corresponding Si and R halides, fission of the Si·Si or Si·O·Si bonds (resulting in the formation of tetrasubstituted monosilanes) occurs. By adding the Si halide to PhNa in light petroleum the fission is largely eliminated. Si_2Ph_6, Si_2Ph_6O, and $SiPhCl_3$ have been prepared. *Hexabenzyldisilane*, m.p. 194°, has been synthesised from Si_2Cl_6 and $CH_2Ph\cdot Na$ or $CH_2Ph\cdot MgCl$. W. R. A.

VII.—PROTEINS.

Further development of the fabric theory of protein structure. D. M. Wrinch (*Phil. Mag.*, 1941, [vii], **31**, 177—198).—There can only be a certain mathematically determinate set of topologically distinct structures made up of amino- and imino-acid residues of the composition ·(NH·CHR·CO)·, with or without units of the composition $(NH_2\cdot CHR\cdot CO)$· and ·$(NH\cdot CHR\cdot CO_2H)$. The problem of protein structure thus becomes the study of all geometrically possible at. patterns satisfying these conditions. Fabrics, or two-dimensional at. patterns, can be built up and folded around to make closed cage-like structures. It is shown that this type of structure will account for the fact that proteins, though megamols., have definite physical and chemical properties, and sp. individualities. Many protein mols. may consist of sets of closed fabric structures in association, which would account for the ease with which they dissociate into simpler proteins. The opposition of polyhedral faces in a fabric cage allows the simultaneous formation of many skeletal H bonds, salt and other linkages. This may explain the formation of protein crystals, and of definite multimol. or micellar structures in the liquid state. Modified cyclol cages, " enol " fabrics, and H-bond fabric cages are considered. A. J. M.

Geometrical attack on protein structure. (Miss) D. M. Wrinch (*J. Amer. Chem. Soc.*, 1941, **63**, 330—333).—The arguments of Pauling and Niemann (A, 1939, II, 461), particularly their thermochemical contentions, are disputed. R. S. C.

Combination of proteins and metaphosphoric acid. G. E. Perlman (*J. Biol. Chem.*, 1941, **137**, 707—711).—HPO_3 combines quantitatively with six representative proteins, the proportion of acid agreeing with the acid-combining power of the proteins estimated in other ways. R. L. E.

Structural formula of the albumin molecule. M. S. Resnitschenko (*Acta Physicochim. U.R.S.S.*, 1940, **12**, 772—782).—The proposed structure is a cylindrical arrangement built up of polypeptide chains in parallel. The cross-linkings are provided for by enolisation, and are so arranged as to give rise to diketopiperazine rings. The applicability of this formula to some aspects of protein chemistry is discussed. F. J. G.

Phosphorylated egg-albumin. M. Heidelberger, B. Davis, and H. P. Treffers (*J. Amer. Chem. Soc.*, 1941, **63**, 498—503).—Treatment of egg-albumin with $POCl_3$–CCl_4 and 3N-NaOH (added in drops as necessary) at −2° to −3° gives phosphated products having a ratio N : P = 5·4 : 1 to 90 : 1. Introduction of the P causes loss of coagulability by heat, greatly increased buffering activity in the neutral range, increase in η, acquisition of precipitability by Ni, Co, and Cd salts, and complete change of immunological specificity with loss of antigenic properties. Part of the P is labile. Denaturation of the albumin also occurs and may account for some of the other changes noted above. R. S. C.

Prosthetic group of sulphhæmoglobin. F. Haurowitz (*J. Biol. Chem.*, 1941, **137**, 771—781).—The formation of sulphhæmoglobin from hæmoglobin by the action of H_2S and O_2 is irreversible. Peptic digestion fails to remove 5—10% of the associated globin, leaving a compound designated *sulphhæminproteose*, which contains 7—10% of S (mainly colloidal). The absorption spectrum of this proteose closely resembles that of protohæmin, and diffusion experiments with alkaline solutions containing 3% of Fe indicate a mol. wt. of ∢19,000. It is insol. in AcOH saturated with HBr, but is hydrolysed by conc. HCl at 100° to a porphyrin, $C_{34}H_{36}O_8N_4S_2$. It probably contains two SO_2 bridges between the porphin nucleus and the side-chains. P. G. M.

Reaction of formaldehyde with proteins. K. H. Gustavson (*Svensk Kem. Tidskr.*, 1940, **52**, 261—277).—The effect of CH_2O on collagen (I) (treated in various ways) at varying p_H has been studied. The source of (I) was limed, de-limed, and trypsin-treated calf skin defatted with $COMe_2$. $\varepsilon\text{-}NH_2$-groups (of lysine) were removed by treatment with HNO_2 for 120 hr. at p_H 2—2·5, followed by maturing for 24 hr. at p_H 4·0 and removal of sol. salts. Guanidyl groups (from arginine) were partly (50%) removed by treatment with NaOCl. Samples were soaked in the appropriate buffer solution for 24 hr. before treatment with CH_2O (2% in the same buffer) for 48 hr. The shrinkage temp. (T_s) was used as a measure of the hardening of the (I). HNO_2-treated (I) does not combine with CH_2O below p_H 8; at p_H 12 the amount combined (0·63 m-equiv. per g. of protein) corresponds with reaction with the guanidyl groups. T_s is not raised by this combination (68° original, 67° after treatment at p_H 12). (I) combines with CH_2O at p_H 6—8 to the amount corresponding with its lysine, and at p_H 12 to its lysine + arginine, content. T_s is increased by treatment at p_H 8, but is not further increased at p_H 12 (69° original, 82° on treatment at p_H 4, 91° at p_H 8, 91° at p_H 12). NaOCl behaves similarly, but the increased CH_2O uptake between p_H 8—12 is only half of that of (I) itself; the T_s increases are similar but slightly larger. 8% CH_2O has no effect on collagen at p_H 1—2, but combination, with increase of T_s, begins at p_H 3. In all cases combination with CH_2O was very much slower below p_H 7. The reaction of $\varepsilon\text{-}NH_2$- and guanidyl groups with CH_2O takes place in both cases at lower p_H than would be expected from the p_H of the corresponding free NH_2-acids. It is concluded that the hardening of (I) by CH_2O is due entirely to the

formation of ·CH_2· bridges between ε-NH_2-groups of different protein mols. and that combination with guanidyl groups has no effect. The structure of (I) is discussed in relation to the above results. M. H. M. A.

Properties of 2-methylthiazoline and their relation to the protein problem. K. Linderstrøm-Lang and C. F. Jacobsen (*J. Biol. Chem.*, 1940, **137**, 443—455).—If the extent of hydrolysis of 2-methylthiazoline (I) at 60° (determined by the action of porphyrindin) is plotted against p_H, the curve closely resembles the ionisation curve, the product being chiefly SH·$[CH_2]_2$·NHAc (indicated by titration to p_H 3), with some SAc·$[CH_2]_2$·NH_2. $[CO_2Et·CH(NH_2)·CH_2·S]_2$ is hydrolysed with liberation of SH groups above p_H 7, ovalbumin below p_H 8, and insulin (after a long induction period) above p_H 10. With NH_4 salts in H_2O, (I) gives SH·$[CH_2]_2$·N:CMe·NH_2, a strong base, stable in acid solution, oxidised by air to $(NH_2·CMe:N·[CH_2]_2·S)_2$ [*chloride*, m.p. 177·5° (corr.); *picrate*, m.p. 184° (corr.)]. Equilibrium consts. are recorded for the reaction between (I) and NH_4 salts in presence of guanidine sulphate, chloride, and bromide, and KCl and KBr. Primary amines react similarly, but *sec.* amines hardly at all. The relation between these reactions and protein denaturation is discussed. A. Li.

Use of optical rotation in study of protein hydrolysis. T. Winnick and D. M. Greenberg (*J. Biol. Chem.*, 1940, **137**, 429—442).—The extent and course of the hydrolysis of casein by nine enzymes and by HCl, and of ovalbumin and edestin by papain and by HCl, have been studied by treating the digest with $CCl_3·CO_2H$, and measuring α, change in NH_2-N, and tyrosine colour val. (Anson) in the filtrate. Results suggest that the course of hydrolysis by different enzymes is the same, but different from that followed by HCl, which results in complete breakdown to NH_2-acids. A. Li.

Effect of the rotation of groups about bonds on optical rotatory power.—See A., 1941, I, 99.

Enzymic proteolysis. IV. Amino-acids of caseinogen phosphopeptone. M. Damodaran and B. V. Ramachandran (*Biochem. J.*, 1941, **35**, 122—134; cf. A., 1939, III, 198).—The presence of 10 NH_2-acids (3 glutamic acid, 3 *iso*leucine, 4 serine) united to three H_3PO_4 residues in the phosphopeptone (A., 1940, II, 317) is confirmed. The phosphopeptone resists the action of trypsin because of the presence of the H_3PO_4 residues, since it is slowly hydrolysed by the enzyme after their removal by 1% alkali. The amounts of total humin-, NH_3-, dicarboxylic acid-, monoamino-, basic-, and non-amino-N in the phosphopeptone are determined. Pyruvic, lactic, and considerable amounts of glyceric acid are formed during hydrolysis of the phosphopeptone with $Ba(OH)_2$. A method for the determination of serine (error 1·5%) in absence of other hydroxyamino-acids by oxidation with chlomirane-T is described. High concn. of serine interferes with the determination of dicarboxylic acids both by titration and by pptn. according to Foreman, in the former by formation of secondary acidic decomp. products, and in the latter because of partial pptn. of serine under the same conditions as the dicarboxylic acids. J. N. A.

Biuret reaction as a titrimetric method, and its application to characterisation of individual proteins. M. I. Plechan (*J. Appl. Chem. Russ.*, 1940, **13**, 620—629).—0·25M-$Cu(OAc)_2$ is added drop by drop to solutions of protein in 0·05N-KOH, shaking after each addition. The end-point is reached when the turbidity equals that given by a drop of aq. $Cu(OAc)_2$ in the same vol. of 0·05N-KOH. The amount of Cu bound is ∝ concn. of protein, but varies for different proteins, according to their content of CO·NH· groups. Thus 1 m-equiv. of Cu^{II} is bound by: biuret 0·107, gelatin 0·274, casein 0·280, serum-albumin 0·200, serum-globulin 0·189, pseudoglobulin 0·188, fibrin 0·212, ovalbumin 0·167 g. R. T.

Determination of tyrosine in protein hydrolysate. T. Laine (*Suomen Kem.*, 1940, **13**, **B**, 18—19).—After removal of aspartic acid (I) by a Foreman pptn., tyrosine (II) is determined by Pucher's malic acid method as for (I) (A., 1939, II, 195). (I) and (II), but not *l*-leucyl-*l*-tyrosine, are the only natural NH_2-acids which can be thus determined. M. H. M. A.

Heat-denaturation of soya glycinin.—See A., 1941, III, 300.

VIII.—ANALYSIS.

Vacuum still for purification of a single substance or recovery of a single fraction.—See A., 1941, I, 133.

Pressure regulator for micro-determination of carbon and hydrogen. J. E. Vance (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 132).—An improved flowmeter for use as a pressure regulator in micro-combustions is described. J. D. R.

Direct determination of oxygen in organic compounds by hydrogenation. I. Optimum analytical conditions. K. Morikawa, T. Kimoto, and R. Abe (*Bull. Chem. Soc. Japan*, 1941, **16**, 1—6; cf. Inaba *et al.*, B., 1936, 580).—The substance should be cracked (Pt—SiO_2) at 950°, and reduced (Ni–ThO_2) at 350°, the streaming velocity being 5 l. per hr. A. Li.

Convenient method for conducting the Kjeldahl digestion.—See A., 1941, I, 133.

Titration of ammonia in presence of boric acid in the macro-, semi-micro-, and micro-Kjeldahl procedures.—See A., 1941, I, 126.

[Determination of] labile sulphur.—See A., 1941, III, 316.

Determination of glycerol in fermentation media containing glucose.—See A., 1941, III, 228.

Segregation of high- and low-titre fatty acids. R. J. de Gray and A. W. de Moise (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 22—24).—Separation of saturated from unsaturated fatty acids is effected by crystallisation from light petroleum at −50°. One crystallisation separates the materials with 95% accuracy, and this may be increased to 99% by a second treatment. The method may be applied to fats themselves, giving an indication of the distribution of the acid mols. on the glycerol, and permitting identification of the free fatty acids in a fat. Apparatus is described and procedure detailed. J. D. R.

Determination of fructose in presence of glucose and sucrose. Ferricyanide method. H. C. Becker and D. T. Inglis (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 13—18).—The mixture is oxidised at 50° for 1 hr. with a reagent containing 50 g. of $K_3Fe(CN)_6$, 225 g. of $Na_2HPO_4,12H_2O$, and 150 g. of Na_2CO_3 per l. Glucose exerts a small but definite reducing action on the reagent, and a factor is introduced to correct this, but sucrose has very little effect and does not interfere appreciably even in large quantities. When the fructose (I) is ⩽20% of the mixture an accuracy of 0·5% is possible, but the error increases rapidly as the concn. of (I) is reduced. Procedure is detailed. J. D. R.

Determination of carotene.—See A., 1941, III, 283.

Polarographic determination of natural products.—See A., 1941, III, 235.

Chemical determination of nicotinic acid. A. Arnold, C. B. Schreffler, and S. T. Lipsius (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 62—63).—The aq. extract of the ground or minced material is heated with NaOH [to free nicotinic acid (I) from its amide], adjusted to p_H 6, and divided into four portions. To two of these, excess of pure (I) is added and to three [including those with excess of (I)], aq. CNBr is added. *p*-$NH_2·C_6H_4·COMe$ is added to all the samples, which are extracted with EtOAc, and colorimetric determinations are made on the EtOAc extracts. The sample with no CNBr is used as blank, and direct comparison of the observed extinction vals. of the other three gives the (I) content of the original sample. J. D. R.

Colour reaction for the pyridine ring, nicotine, and anabasine, and the colorimetric determination of these alkaloids. A. Schmuk and A. Borozdina (*J. Appl. Chem. Russ.*, 1940, **13**, 776—782).—5% KCNS is added to aq. Br to decolorisation. 1 ml. of this solution of BrCNS and 1 ml. of aq. NH_2Ph are added to the test solution, when an intense yellow coloration develops in presence of nicotine (I) and other compounds of C_5H_5N. Addition of 1 ml. of 2% Na_2CO_3 and H_2O to 100 ml. does not affect the colour in the cases of (I), nicotinic acid, and C_5H_5N, but changes it to pink in the case of anabasine (⩽0·5 mg.), and to greenish-yellow in the case of nicotyrine. The concn. of a given alkaloid is then determined colorimetrically, by comparison with standards. The method is not applicable to mixtures of C_5H_5N alkaloids. R. T.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

MAY, 1941.

I.—ALIPHATIC.

Hyperconjugation.—See A., 1941, I, 100.

Homologous series of alkanes. Density and its temperature coefficient.—See A., 1940, I, 106.

Isolation and properties of αα-dineopentylethylene, a component of tri*iso*butylene. P. D. Bartlett, G. L. Fraser, and R. B. Woodward (*J. Amer. Chem. Soc.*, 1941, **63**, 495—498). —~50% of tri*iso*butylene (I) is unaffected by an excess of $KMnO_4$ in aq. KOH at 100°. The residual material is *ββζζ-tetramethyl-δ-methylene*-n-*heptane* (II), b.p. 177·7—178·0°/760 mm., 85—86°/40 mm. Other constituents of (I) give $Bu^{\gamma}CO_2H$ (III) and $CMe_2(CO_2H)_2$ [obtained from (III) by $KMnO_4$]. (II) is indifferent to H_2–PtO_2 in dioxan, EtOH, or AcOH; with Br in CCl_4 it evolves HBr; it is oxidised by $K_2Cr_2O_7$ in strong acid. With H_2–Raney Ni at 150°/~130 atm., (II) gives $CHMe(CH_2Bu^{\gamma})_2$, b.p. 179—180°, which is oxidised at the $\geq$CH by $KMnO_4$. With BzO_2H in $CHCl_3$, (II) readily gives an *oxide* (IV), b.p. 85—88°/15 mm., rearranged by aq. H_2SO_4 to an aldehyde, which by autoxidation gives $CH(CH_2Bu^{\gamma})_2{\cdot}CO_2H$, m.p. 87—88° (amide, m.p. 139—140°), obtained also directly from (IV) by $K_2Cr_2O_7$. R. S. C.

Preparation of chloroform. O. L. Baril (*J. Chem. Educ.*, 1940, **17**, 565—566).—An improved laboratory method giving an 80—85% yield from bleaching powder and $COMe_2$ is described. L. S. T.

Reactions of atoms and free radicals in solution. I. Substitution of hydrogen on an asymmetric carbon atom. Chlorination of primary active amyl chloride. H. C. Brown, M. S. Kharasch, and T. H. Chao. **II. Non-isomerisation of free alkyl radicals in solution.** M. S. Kharasch, S. S. Kane, and H. C. Brown (*J. Amer. Chem. Soc.*, 1940, **62**, 3435—3439; 1941, **63**, 526—528).—I. Photochemical or catalysed (Bz_2O_2) chlorination of (+)-CHMeEt·CH_2Cl gives *dl*-CMeEtCl·CH_2Cl (I), b.p. 71·5°/100 mm., (+)-*αα-dichloro-β-methylbutane*, b.p. 76±2°/100 mm., $[\alpha]_D^{23}$?+2·2°, (−)-, b.p. 89·2°/100 mm., $[\alpha]_D^{23}$ −7·05°, and (+)-CH_2Cl·CHMe·CHMeCl, b.p. 91°/100 mm., $[\alpha]_D^{23}$ +5·70°, (−)-CH_2Cl·CHMe·$[CH_2]_2$·Cl, b.p. 101—102°/100 mm., and *α-chloro-β-chloromethylbutane*, b.p. 89—91°/100 mm. The inactivity of (I) proves that reaction occurs by way of the org. radical and not by attack at the " back " of the C affected. Presence of (I) is confirmed by the rate of hydrolysis by 0·02N-NaOH in 80% EtOH, which closely resembles that of $CMe_2Cl{\cdot}CH_2Cl$ (in both cases only the *tert.* C is affected). The results also confirm correlation of (+)-CHMeEt·CH_2·OH with (+)-$CO_2H{\cdot}CHMe{\cdot}CH_2{\cdot}CO_2H$, *d*(+)-$CO_2H{\cdot}CH_2{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}CO_2H$, (+)-citronellal, etc.

II. In boiling CCl_4, $(RCO_2)_2$ undergo the reactions: $(RCO_2)_2 \rightarrow 2R + 2CO_2$; $R + CCl_4 \rightarrow RCl + CCl_3$; $2CCl_3 \rightarrow C_2Cl_6$. Isolation of pure $Pr^{\alpha}Cl$ and $Pr^{\beta}Cl$ from $(Pr^{\alpha}CO_2)_2$ and $(Pr^{\beta}CO_2)_2$ (preps. described), respectively, shows that, contrary to Glazebrook *et al.* (A., 1937, II, 43), no isomerisation of Pr radicals occurs. Some $PrCO_2Et$ is formed in each case by decomp. to RCO_2 and reaction thereof with Et_2O. R. S. C.

Reaction between maleic anhydride and isomerides of piperylene. R. F. Robey, C. E. Morrell, and H. K. Wiese (*J. Amer. Chem. Soc.*, 1941, **63**, 627—628).—When piperylene, obtained by cracking petroleum oil or dechlorinating $C_5H_{10}Cl_2$, is passed in H_2 through molten $(CH{\cdot}CO)_2O$, there are obtained small amounts of unreactive (? *cis*) form, b.p. 43·8°. R. S. C.

Cleavage of diethyl ether by hydrogen bromide. F. R. Mayo, W. B. Hardy, and C. G. Schultz (*J. Amer. Chem. Soc.*, 1941, **63**, 426—436).—EtOH (formed during the reaction) and H_2O accelerate cleavage of Et_2O by HBr in Et_2O or PhMe, retard it in AcOH, and have little effect in $CHCl_3$. These effects are eliminated by addition of AcBr. The reaction is then of first order with respect to Et_2O and of second order with respect to HBr in PhMe, PhCl, or Et_2O, of $\frac{3}{2}$ and first order with respect to both reactants in $CHCl_3$ or AcOH, respectively. Reaction mechanisms, discussed in detail, involve mixed six-membered rings. R. S. C.

Danger of peroxide formation. J. B. Culbertson (*J. Chem. Educ.*, 1940, **17**, 595).—The formation of an explosive material from Pr^{β}_2O on storage is described. L. S. T.

Polyhydric alcohol–polybasic acid reaction. VI. Glyceryl adipate and sebacate polyesters. R. H. Kienle and F. E. Petke (*J. Amer. Chem. Soc.*, 1941, **63**, 481—484; cf. A., 1940, II, 266). —Changes in acid no. and the H_2O evolved as glycerol reacts with $CO_2H{\cdot}[CH_2]_n{\cdot}CO_2H$ (*A*) ($n = 4$) at 190° indicate that only interesterification occurs and that ~30% of tetrameride or higher polymeride has been formed when gelation occurs, at which stage some H ester is still present. Results for (*A*) ($n = 6$) are similar, but a little intraesterification also occurs. Results for *o*-$C_6H_4(CO_2H)_2$ and (*A*) ($n = 2$, 4, and 6) are compared. R. S. C.

Oxidation of alkyl tellurides. M. P. Balfe and K. N. Nandi (*J.C.S.*, 1941, 70—72).—Equimols. of di-*n*-amyl telluride (I) and MeI, $CH_2Br{\cdot}CO_2Et$, or CH_2BzBr afford methyldi-*n*-amyltelluronium iodide, m.p. 70°, the *Et* ester (II), m.p. 50°, of di-*n*-amyltelluretine bromide, or phenacyldi-*n*-amyltelluronium bromide, m.p. 84°, respectively. Thermal decomp. of (II) yields *Et* n-*amyltelluroacetate* (III), b.p. 140—150°/17 mm., converted by Bz_2O_2–$CHCl_3$ into the *dibenzoate*, $C_5H_{11}{\cdot}Te(OBz)_2{\cdot}CH_2{\cdot}CO_2Et$, m.p. 77—78°. (I) and *l*-menthyl bromoacetate give an impure product, decomposed to *n*-$C_5H_{11}Br$ and *l*-menthyl *n*-amyltelluroacetate (IV), b.p. 78—85°/17 mm., Equimols. of (I) and $HgCl_2$ or HgI_2 give impure products, but $HgBr_2$ yields an *adduct*, m.p. 88°. (I) or (III) and I–$CHCl_3$ or –CCl_4 afford viscous products. (I), (III), or (IV) exposed to air affords n-*amyltellurinic acid*, decomp. 200—220°. (I) and H_2O_2 give a *complex*, $3[(C_5H_{11})_2TeO],C_5H_{11}{\cdot}TeO_2H$, m.p. 144° (decomp.), or in $COMe_2$ solution, a similar product, m.p. 152° (decomp.). (III) and H_2O_2 afford a *complex*, $C_5H_{11}{\cdot}TeO{\cdot}CH_2{\cdot}CO_2Et,2C_5H_{11}{\cdot}TeO_2H$, decomp. 200°. Bu^{γ}_2 telluride could not be obtained pure. A. T. P.

Products obtained by heating ricinoleic acid and its mixtures with oxalic acid. V. I. Esafov and A. V. Schpadi (*J. Appl. Chem. Russ.*, 1940, **13**, 1040—1044).—Estolides are produced by heating ricinoleic acid (I) at 200°; the mean mol. wt. rises gradually from 617 after 2 hr. to 1480 after 64 hr. Heating of 1 : 2 and 2 : 1 (I)–$H_2C_2O_4$ mixtures leads to formation of polymerised, bridged oxalates. R. T.

Synthesis of radioactive lactic acid. R. D. Cramer and G. B. Kistiakowsky (*J. Biol. Chem.*, 1941, **137**, 549—555).—Lactic acid containing a trace of $OH{\cdot}CHMe{\cdot}{}^{11}CO_2H$ is synthesised as follows. B_2O_3 is bombarded with deuterons and then heated with $CaCO_3$, the evolved CO_2 heated at 525° in a sealed tube with NH_3 and excess of K, the product treated with excess of MeCHO, the resulting nitrile hydrolysed by conc. HCl at 100°, and the acid purified by Et_2O extraction. CO_2 containing $^{11}CO_2$ is converted via Na and Ba carbonates, BaC_2, C_2H_2, MeCHO and its cyanohydrin into lactic acid containing $OH{\cdot}{}^{11}CHMe{\cdot}CO_2H$ and $^{11}CH_3{\cdot}CH(OH){\cdot}CO_2H$. A. Li.

Structure of phellonic acid. N. L. Drake, H. W. Carhart, and R. Mozingo (*J. Amer. Chem. Soc.*, 1941, **63**, 617—620).—

Phellonic acid (**I**) (isolation described), m.p. 93—93·5°, is proved to be *χ-hydroxytetracosanoic acid*. It contains 2 active H and consumes 4 MgMeI. With KOH at 250°, rising to 350°, it gives CO_2 and $CO_2H{\cdot}[CH_2]_{18}{\cdot}CO_2H$ (**II**), m.p. 122·5—124·5°. Electrolysis of $CO_2Et{\cdot}[CH_2]_8{\cdot}CO_2Na$ gives $CO_2Et{\cdot}[CH_2]_{16}{\cdot}CO_2Et$, hydrogenated (Cu chromite; 250°/3000—4000 lb.; dioxan) to $OH{\cdot}[CH_2]_{18}{\cdot}OH$, m.p. 96—97°. The derived (HBr; 135—140°) dibromide, m.p. 60—61°, with $CHNa(CO_2Et)_2$ in boiling PhMe yields *Et*$_4$ *eicosane-aavv-tetracarboxylate*, m.p. 43—44°, converted by NaOH in $(OH{\cdot}[CH_2]_2)_2O$ at 100° into (**II**). The *Me*$_2$ ester, m.p. 68—69°, of (**II**) with Na ribbon in C_6H_6 gives *αχ-docosamethylene glycol*, m.p. 105·7—106·2°, and with KOH–MeOH–C_6H_6 gives the *Me H* ester, m.p. 82·5—84°, which with $SOCl_2$–PhMe, followed by ZnEt$_2$, gives an impure keto-ester, hydrogenated (Cu chromite; 150°/2800 lb.; MeOH) to Me phellonate, m.p. 73·8—74·8° [gives (**I**), m.p. 92·8—94·3°, by hydrolysis], and a substance, m.p. 93·5—99°. R. S. C.

Polymorphism of C_{18} unsaturated acids.—See A., 1941, I, 159.

Rates of oxidation of isomeric di- and tetra-hydroxystearic acids by lead tetra-acetate. T. P. Hilditch and H. Jasperson (*Nature*, 1941, **147**, 327).—Measurements of the rate of consumption of $Pb(OAc)_4$ used to oxidise isomeric polyhydroxystearic acids show marked differences between the speeds of oxidation of isomeric forms. Data for the two Δ^0-dihydroxy-acids oxidised in glacial AcOH at 20° are recorded. The rate for the acid of m.p. 95° is $\gg$ that of the isomeride, m.p. 132°. L. S. T.

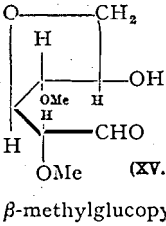
Oxidation of aldehydes with hydrogen peroxide. J. H. Payne and G. F. Lemon, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 226—228).—H_2 is produced in the oxidations of pivalaldehyde and of glycollaldehyde by H_2O_2 at 95° but not with glyoxal and PhCHO. If CH_2O is formed as an intermediate product during the oxidation of a particular compound H_2 will appear among the oxidation products. W. R. A.

Aldol and constitution of *p*-aldol. M. Hori (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 1—5).—Aldol combines with $NaHSO_3$ in acid solution and is liberated again by alkali. *p*-Aldol is probably $CH_2<^{CH(OH)\cdot O\cdot CHMe}_{CHMe\cdot O\cdot CH(OH)}>CH_2$. J. N. A.

Nature of complex formation between boric acid and organic polyhydroxy-compounds. Y. Tsuzuki (*Bull. Chem. Soc. Japan*, 1941, **16**, 23—31).—Measurements of changes in [α] show that borates (in accordance with the extent of ionisation) form complexes to a large extent with mannitol and glucose, while H_3BO_3 has little effect. Both H_3BO_3 and borates readily form complexes with tartaric acid, tartrates, and Ca gluconate, but those formed in acid medium have different structures from those formed in alkaline medium. A. Li.

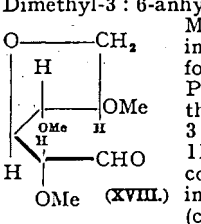
Preparation and physical properties of 1-chloroglucose 2 : 3 : 4 : 6-tetra-*p*-toluenesulphonate. A. L. Bernoulli and H. Stauffer (*Helv. Chim. Acta*, 1940, **23**, 615—626).—Glucose (1 mol.) in C_5H_5N (40 mols.) and p-$C_6H_4Me{\cdot}SO_2Cl$ (10 mols.) in $CHCl_3$ at room temp. for 5 days afford 1-*chloroglucose* 2 : 3 : 4 : 6-*tetra*-p-*toluenesulphonate* (**I**), m.p. 78—80° (gradual decomp.), $[\alpha]_D^{20}$ +61·89° in $CHCl_3$ (probably *α-cis* form), converted by refluxing with Ag_2O–MeOH into β-1-methyl-*d*-glucoside 2 : 3 : 4 : 6-tetra-*p*-toluenesulphonate, m.p. 177—178° (cf. Oldham *et al.*, A., 1932, 500). Absorption curves of (**I**) agree with its constitution; comparison is made with p-$C_6H_4Me{\cdot}SO_3Me$. Dipole moments are measured. A. T. P.

Properties of 3 : 6-anhydroglueose. W. N. Haworth, L. N. Owen, and F. Smith (*J.C.S.*, 1941, 88—102; cf. A., 1940, II, 244).—In 3 : 6-anhydroglucose and its derivatives, the 3 : 6-anhydro-ring acquires the character of the principal ring to which the pyranose and furanose ring is subsidiary. The 3 : 6-anhydro-ring governs the structure of these substances and appears to be mainly responsible for their peculiar properties. Such novel changes as are outlined below do not occur in the case of pyranosides and furanosides which contain no anhydro-ring. 1 : 2-*iso*Propylidene-3 : 6-anhydroglucofuranose (**I**) and Purdie's reagents give 1 : 2-iso*propylidene-5-methyl*-3 : 6-*anhydroglucofuranose* (**II**), b.p. 115°/0·03 mm. (all b.p. are bath temp.) (*semihydrate*, m.p. 43—44°, $[\alpha]_D^{18}$ +82° in EtOH), converted by 0·1N-H_2SO_4–EtOH at 90° into 5-methyl-3 : 6-anhydroglucose (**III**), oxidised by HNO_3 (*d* 1·2) at 50° to 5-*methyl*-3 : 6-*anhydro-γ-gluconolactone*, b.p. 165—170°/0·02 mm., $[\alpha]_D^{18}$ +109° → +71° in H_2O in 240 hr. (*Na* salt, $[\alpha]_D^{18}$ +28° in H_2O; after acidification the solution has $[\alpha]_D^{18}$ +31° → +60° in 261 hr.; acid *amide*, m.p. 136—137°, $[\alpha]_D^{20}$ +68° in H_2O, gives a positive Weerman test). (**II**) or (**III**) and boiling 2% HCl–MeOH afford 5-*methyl*-3 : 6-*anhydromethylglucofuranoside* (can exist only as furanoside), methylated further to the 2 : 5-*Me*$_2$ compound (**IV**), b.p. 90—95°/0·03 mm., which is hydrolysed by 0·1N-H_2SO_4 at 100° (bath) to 2 : 5-*dimethyl*-3 : 6-*anhydroglucose* (**V**), b.p. 120°/0·04 mm., $[\alpha]_D^{18}$ +110° → +120° in H_2O in 60 hr. [*anilide* (**VI**), m.p. 96°, $[\alpha]_D^{18}$ +143° in EtOH]. (**V**) and Br–H_2O at 40° for 3 days yield 2 : 5-*dimethyl*-3 : 6-*anhydro-γ-gluconolactone* (**VII**), b.p. 130—135°/0·02 mm., $[\alpha]_D^{18}$ +96° → +73° in H_2O (const.) after 200 hr. [corresponding *amide* (**VIII**), m.p. 92°, $[\alpha]_D^{19}$ +41° in H_2O; (**VIII**) and (**VI**) were described previously (Peat *et al.*, A., 1938, 348) as derivatives of 2 : 4-dimethyl-3 : 6-anhydroglucose]. (**I**) and 0·1N-H_2SO_4 at 100° (bath) give 3 : 6-anhydroglucose (**IX**), oxidised by aq. Br at room temp. for 6 days to 3 : 6-anhydro-γ-gluconolactone, m.p. 116° (corresponding amide, m.p. 160°, $[\alpha]_D^{15}$ +109° in H_2O), methylated to impure (**VII**), converted into (**VIII**). (**IX**) with 1% MeOH–HCl at room temp. shows a change of $[\alpha]_D$ +47° to +56° (const.) in 1 hr.; boiling gives no further change in $[\alpha]_D$, and the mixture affords α- + β-3 : 6-anhydromethylglucofuranoside (**X**), b.p. 140—150°/0·04 mm., $[\alpha]_D^{18}$ +38° in H_2O, methylated to (**IV**), and thence hydrolysed by 5% HCl at 20° to (**V**), and converted into (**VII**) and (**VIII**). Neither the amide (see later) nor the NH_4 salt of 2 : 4-dimethyl-3 : 6-anhydrogluconic acid is detected, and thus the mixture of glucosides prepared from the 3 : 6-anhydroglucose with HCl–MeOH must be methylfuranosides. (**X**) in 0·1N-H_2SO_4 at room temp. gives $[\alpha]_D^{18}$ +38° → +52° in 104 days; mechanical separation affords 3 : 6-*anhydro-α-methylglucofuranoside* (**XI**), m.p. 70°, $[\alpha]_D^{20}$ +164° in H_2O (changed in 0·1N-H_2SO_4 to +126° in 40 days), and -β-methylglucofuranoside (**XII**), m.p. 98°, $[\alpha]_D^{20}$ −54° in H_2O, changing in 0·1N-H_2SO_4 to −4° in 45 days (cf. Ohle *et al.*, A., 1939, II, 8). (**XI**) is methylated (Purdie) to 2 : 5-*dimethyl*-3 : 6-*anhydro-α-methylglucofuranoside*, m.p. 45°, $[\alpha]_D^{18}$ +208° in H_2O, hydrolysed by 0·1N-H_2SO_4 at 100° (bath) [$[\alpha]_D$ changes to +112° (const.) in 4·5 hr.] to 2 : 5-dimethyl-3 : 6-anhydroglucofuranose, which affords (**VI**), and also (as above) (**VII**) and (**VIII**). (**XII**) yields 2 : 5-dimethyl-3 : 6-anhydro-β-methylglucofuranoside, b.p. 100°/0·04 mm., $[\alpha]_D^{18}$ +15° in H_2O, converted [100°; $[\alpha]_D$ +104° (const.) in 5·5 hr.; hydrolysis at room temp. is incomplete in 45 days] into the anhydroglucose and subsequently into (**VI**), (**VII**), and (**VIII**). α-Methylglucopyranoside and CPh_3Cl–C_5H_5N at room temp., then at 40°, afford the 6-CPh_3 derivative, acetylated (Ac_2O–C_5H_5N) at room temp. to the 2 : 3 : 4-triacetate, m.p. 136°, and treatment with HBr–AcOH then gives α-methylglucopyranoside 2 : 3 : 4-triacetate, m.p. 110°, converted into the 6-p-$C_6H_4Me{\cdot}SO_2$ derivative, m.p. 86°, $[\alpha]_D^{18}$ +126° in $CHCl_3$, and thence (Na–MeOH) into 3 : 6-anhydro-α-methylglucopyranoside (**XIII**), m.p. 108°, $[\alpha]_D^{20}$ +56° in H_2O. (**XIII**) is converted into the furanoside (**XI**), without affecting the spatial arrangement of the groups (H and OMe) at $C_{(1)}$, by means of MeOH–HCl or HCl–Et_2O–$CHCl_3$ (almost instantaneously), or more slowly by 0·1N-H_2SO_4 at room temp. for 16 hr. ($[\alpha]_D$ increases to +145°). Prolonged treatment of (**XIII**) with 1% MeOH–HCl shows $[\alpha]_D^{19}$ +50° (const.) in 12 hr. and the mixture affords (**X**), converted into (**V**), and thence into (**VI**) or (**VIII**). Methylation (Purdie) of (**XIII**) gives 4-*methyl*-3 : 6-*anhydro-α-methylglucopyranoside*, m.p. 152° $[\alpha]_D^{17}$ +24° in H_2O, which gives (0·1N-H_2SO_4) 4-*methyl* 3 : 6-*anhydroglucose*, $[\alpha]_D^{18}$ −17° in H_2O, converted by aq. Br at room temp. into 4-*methyl*-3 : 6-*anhydrogluconic acid* (*Me* ester, b.p. 125°/0·03 mm., $[\alpha]_D^{19}$ ~+2° in H_2O; *amide*, $[\alpha]_D^{20}$ −7·5° in H_2O). Further methylation of (**XIII**) or the 4-Me compound affords the 2 : 4-*Me*$_2$ derivative (**XIV**), m.p. 66°, $[\alpha]_D^{16}$ +50° in H_2O. (**XIV**) in 0·1N-H_2SO_4 at room temp. shows a change in $[\alpha]_D$ of +43° to −20° (const. after 8 hr.), and 2 : 4-*dimethyl*-3 : 6-*anhydroglucose* (**XV**), b.p. 120—125°/0·03 mm., $[\alpha]_D^{19}$ −28° in H_2O, is obtained, which is converted by aq. Br at 40—45° for 3 days into 2 : 4-*dimethyl*-3 : 6-*anhydrogluconic acid*, m.p. 156°, $[\alpha]_D^{20}$ +52° in H_2O (sublimes unchanged at 140°/0·04 mm.) (Me ester and NH_3–MeOH give the *amide*, m.p. 155°). β-Methylglucopyranoside 6-bromohydrin 2 : 3 : 4-triacetate is deacetylated (Na–MeOH) and the product then heated at 85—90° with N-NaOH to give 3 : 6-anhydro-β-methylglucopyranoside (**XVI**), b.p. 160—170°/0·02 mm.



(XV.)

$[\alpha]_D^{20}$ −138° in H_2O (m.p. in sealed tube ~50°), which is transformed into (**XII**) by 1% MeOH–HCl (4 min.) or HCl–Et_2O–$CHCl_3$ [reaction is arrested to prevent formation of α + β-form (**X**)]. (**XVI**) is hydrolysed slowly by 0·1N-H_2SO_4 at room temp.; $[\alpha]_D$ is −18° after 17 hr. and 3 : 6-anhydroglucose is obtained, but no (**XII**). (**XII**) is methylated (Purdie's reagents) to 2 : 4-*dimethyl*-3 : 6-*anhydro*-β-*methylglucopyranoside* (**XVII**), b.p. 85—90°/0·01 mm., $[\alpha]_D^{15}$ −96° in H_2O, hydrolysed by 0·1N-H_2SO_4 more slowly than is (**XIV**) (α-form), to give (**XV**). (**XIV**) is transformed at room temp. in a sealed tube for 4 months, or more rapidly in air (+ a trace of HCl), into (**XVII**); there is partial transformation of the α- into the β-form during methylation of (**XIII**). 2 : 4-Dimethyl-3 : 6-anhydro-αβ-methylglucopyranoside in 0·5% MeOH–HCl at room temp. shows a change in $[\alpha]_D$ of −14° to +8° in 3·5 hr. (const. for 15 hr.). Successive treatment with Purdie's reagents and MeOH–HCl converts the resulting syrup into 2 : 4 : 5-*trimethyl*-3 : 6-*anhydroglucose* *Me*$_2$ *acetal*, b.p. 110—120°/0·01 mm., $[\alpha]_D^{18}$ −6° in H_2O (may contain some unchanged material), which in 0·1N-H_2SO_4 at room temp. for 14 hr. (const. val. of $[\alpha]_D$ −14°) affords 2 : 4 : 5-*trimethyl*-3 : 6-*anhydro*aldehydo*glucose* (**XVIII**), b.p. 105—110°/0·01 mm. A. T. P.


(XVIII.)

Action of diazomethane on acyclic sugar derivatives. M. L. Wolfrom, D. I. Weisblat, and S. W. Waisbrot (*J. Amer. Chem. Soc.*, 1941, **63**, 632).—*keto-d*-Fructose penta-acetate with CH_2N_2 and a trace of MeOH in $CHCl_3$ give the *compound*, $OR{\cdot}CH_2{\cdot}[CH(OR){\cdot}]_3{\cdot}C(CH_2{\cdot}OR)\langle_{O}^{CH_2}$ (**I**) (R = Ac), m.p. 86—87°, $[\alpha]_D^{24}$ +32° in $CHCl_3$, hydrolysed by $Ba(OMe)_2$ to the *oxide* (**I**) (R = H), m.p. 136°; both products reduce Tollens' reagent but give no colour with KOH–MeOH. 1-Diazo-1-deoxy-*keto-d*-glucoheptulose penta-acetate with HCl–Et_2O or HBr–Et_2O gives 1-*chloro*-, m.p. 100—101°, $[\alpha]_D^{22}$ −5·5° in $CHCl_3$, and 1-*bromo*-keto-d-*glucoheptulose penta-acetate*, m.p. 86—87°, $[\alpha]_D^{24}$ −4° in $CHCl_3$, respectively, and with Ag_2O in hot H_2O gives 2-*deoxy*-d-*glucoheptonolactone tetra-acetate*, m.p. 129—130°, $[\alpha]_D^{20}$ +39·5° in $CHCl_3$, hydrolysed by $Ba(OH)_2$ to the free *lactone*, m.p. 170°, $[\alpha]_D^{20}$ +20° in H_2O. R. S. C.

Action of formic acid on starch. D. Gottlieb, C. G. Caldwell, and R. M. Hixon (*J. Amer. Chem. Soc.*, 1940, **62**, 3342—3344).—In 90% HCO_2H at room temp. maize starch gives a 6-*formate* (**I**), $[\alpha]_D^{25}$ +2·09° to +2·16° in C_5H_5N. Longer interaction gives only slightly higher formylation. At 85° hydrolysis occurs and a *dextrin monoformate* is obtained. (**I**) gives a red colour with I, but hydrolysis regenerates a starch giving the blue colour. HIO_4 oxidises (**I**) to a *formate*, $(C_7H_8O_6)_n$, hydrolysis of which by, first, boiling H_2O and then N-HCl at 99° gives glyoxal. With Ac_2O–C_5H_5N, (**I**) gives a *formate diacetate* and with *p*-$C_6H_4Me{\cdot}SO_2Cl$–C_5H_5N gives a *formate di*-p-*toluenesulphonate*, which with 32% HBr–AcOH gives bromodiacetylglucose di-*p*-toluenesulphonate. R. S. C.

Linking between the repeating units in the starch molecule. C. C. Barker, E. L. Hirst, and G. T. Young (*Nature*, 1941, **147**, 296).—Experiments showing that in the derivatives of starch examined the OH concerned in the glucosidic union of the repeating units (cf. A., 1940, II, 338) is a primary alcoholic group situated at $C_{(6)}$ of one of the glucose residues are recorded. L. S. T.

Structure of starch granules. R. Haller (*Helv. Chim. Acta*, 1940, **23**, 596—606).—The influence of oxidising agents on the structure of the starch granule is examined. The study is limited to the use of aq. NaOCl or Br–$CaCO_3$ at room temp.; other agents, *e.g.*, $KMnO_4$, 1% aq. $NaBO_3$ or $Na_2S_2O_8$, 1% aq. CaO_3 or 10% aq. H_2O_2 at 50°, are less satisfactory. Starch modified by the NaOCl process gives an apparently homogeneous blue-violet colour with KI_3. Variations are then noticed with the use of swelling agents, *e.g.*, $CCl_3{\cdot}CH(OH)_2$, CuO–$(CH_2{\cdot}NH_2)_2$ (reagent *A*), $Ca(NO_3)_2$, or NaI, when the granule becomes deformed and the colour localised. Colour reactions are recorded in detail and photomicrographs are shown. The granules after treatment with (*A*) show a brown nucleus from which colourless membranes radiate, and later the nucleus breaks down to a cloud of minute particles, leaving a system of membranes insol. in the reagent. If the modified granules are treated with Ag solutions and allowed to swell with conc. aq. NaI, microscopical examination shows that the layers are not changed in the same manner as the substance enclosed between them. Similar results are noticed with starch treated with Br–$CaCO_3$. Such granules are dyed intensely with Ru-red (**II**), and with (*A*) then show the swelling phenomena clearly. Native starch is only slightly coloured with (**II**) and on swelling does not show the lamellar structure. Previously, stratification was explained by difference in H_2O content, but oxidation experiments indicate a structure which is not homogeneous, the substance between the layers being sol. in certain alkaline reagents, *e.g.*, (*A*) or aq. NaOH. Meyer's view of the structure of starch granules as intermingling units of α- and β-amylose may hold for the interlamellar substance. A. T. P.

***p*-Toluenesulphonation of cellulose.** A. L. Bernoulli and H. Stauffer (*Helv. Chim. Acta*, 1940, **23**, 627—649).—There is a relationship between *p*-toluenesulphonation and degradation of cellulose (**I**). (**I**) is not esterified by $(p\text{-}C_6H_4Me{\cdot}SO_2)_2O$ in C_5H_5N at room temp. at normal pressure or 20 atm. *p*-Toluenesulphonation of (**I**) (1 mol.) by C_5H_5N (40—60 mols.) at 70°, then *p*-$C_6H_4Me{\cdot}SO_2Cl$ (**II**) (10—15 mols.) at room temp., is confirmed (cf. Hess *et al.*, A., 1933, 1280). Reaction in large excess of C_6H_6 or in presence of MgO (4 mols.) is inhibited. The use of 3, 4, or 5 mols. of (**II**) at room temp. or at 90° gives no esterification, except slightly with 5 mols. at 90°. (**I**) (1 mol.) with C_5H_5N,HCl (3 mols.) and C_5H_5N (37 mols.) for 4 days, then (**II**)–MgO, gives some esterification. Hydrocellulose, cellobiose, or glucose is esterified in presence or absence of MgO. It is not certain whether this is due to a shortening of the length of chain or to physical condition. The yield of ester ∝ Cu no. through a max. and then compounds of higher Cu no. give a lower yield of ester (due to presence of EtOH-sol. esters). (**II**) (12 mols.) in $CHCl_3$ added to cellobiose (1 mol.) at −15°, then at room temp., yields a compound (**III**), begins to melt at 92°, allied to a monochlorocellobiose tetra-*p*-toluenesulphonate, apparently not homogeneous. (**I**) (1 mol.) is esterified by BzCl (10 mols.)–C_5H_5N (7 days at room temp.) and to a smaller extent in presence of MgO. Absorption curves of (**III**) and cellulose *p*-toluenesulphonate are recorded; the dipole moment of the latter is given. A. T. P.

Polyhydroxy-acyl derivatives of β-alanine. T. Reichstein and A. Grüssner (*Helv. Chim. Acta*, 1940, **23**, 650—657).—Aldol and aq. NaCN–$CaCl_2$ at 0°, then at room temp., followed by boiling with aq. NaOH, afford αγ-dihydroxyvalerolactone (**I**), b.p. 89°/0·2 mm. (amide, m.p. 103—105°), which is a mixture of *d*- and *l*-forms. Allylacetic acid and $AgClO_3$–OsO_4 afford γδ-dihydroxyvalerolactone, b.p. 100°/0·1 mm., purified through the *Cd* salt. $Cl{\cdot}[CH_2]_3{\cdot}CBr(CO_2Et)_2$–aq. NaOH–EtOH, refluxed for 12 hr., yield *dl*-αδ-dihydroxyvalerolactone (**II**), b.p. 70°/0·1 mm., 123—125°/10 mm. (phenylhydrazide, m.p. 106—107°). *dl*-α-Hydroxy-ββ-dimethylbutyrolactone (**III**), m.p. 75—78° [*amide* (**IV**), m.p. 123—124°], and quinine in EtOH afford quinine salts, m.p. 186—187° and 174—175°, respectively, converted by aq. $Ba(OH)_2$ into the l- (**V**), m.p. 80—85°, $[\alpha]_D^{15}$ −15·3°±2° in $COMe_2$ [amide, m.p. 124—124·5°, depressed by (**IV**) to 118—120°], and d-*lactone*, m.p. 78—80° (sinters at 70°), $[\alpha]_D^{17}$ −11·3°±2° in $COMe_2$ (amide, m.p. 124—124·5°, $[\alpha]_D^{17}$ 0°±2° in MeOH), respectively. (**I**) or (**II**) and β-alanine Me ester in MeOH (reflux for 1 hr.) give αγ- (**VI**), b.p. 135—140°/0·001 mm., or dl-αδ-*dihydroxyvaleroyl*-β-*alanine Me ester* (**VII**), b.p. 135°/0·001 mm. (**III**) similarly affords dl-αγ-*dihydroxy*-ββ-*dimethylbutyroyl*-β-*alanine Me ester* (**VIII**) (Me *dl*-pantothenate), b.p. 130°/0·001 mm. (**V**) yields a similar ester, $[\alpha]_D^{15}$ +37·1° in $COMe_2$ (partial racemisation may occur). For biological tests, the esters are hydrolysed by aq. NaOH at room temp. With a certain bacterium, (**VI**) and (**VII**) and their corresponding acids are inactive, whereas (**III**) and (**VIII**) show good activity, especially with addition of nicotinamide. A. T. P.

Physicochemical studies of the simpler polypeptides.—See A., 1941, I, 167.

Synthesis of *S*-(β-amino-β-carboxyethyl)homocysteine. G. B. Brown and V. du Vigneaud (*J. Biol. Chem.*, 1941, **137**, 611—615).—Homocysteine or its Na salt (from the *S*-CH_2Ph derivative and Na in liquid NH_3) with KOH and $CH_2Cl{\cdot}CH(NH_2){\cdot}CO_2H$ or its Me ester (from serine by a modification of the method of Fischer *et al.*, A., 1907, i, 900) in absence of O_2 yields *S*-(β-amino-β-carboxyethyl)homocysteine (Küster *et al.*, B., 1929, 937; Horn *et al.*, A., 1940, II,

461) (probably a mixture of two *dl*-forms), decomp. 270° [NN'-*dicarbobenzyloxy*-derivative, m.p. 108—111° (slow decomp.)], which with conc. HI gives small amounts of homocysteine thiolactone and cysteine. A. Li.

Amino-sulphonic acid analogues of natural amino-carboxylic acids. H. McIlwain (*J.C.S.*, 1941, 75—77).—Many substances which inhibit growth of micro-organisms appear to do so by interfering with substances of similar structure which are essential in reactions involving growth. The following inhibiting amino-sulphonic acids, related to natural α-NH_2-acids or β-alanine, are prepared from aq. NH_3 and the respective aldehyde–H sulphite compound: *α-amino*iso*butane*- (**I**), *α-amino*iso*pentane*- (**II**), and *α-aminophenylmethanesulphonic acid* (**III**), m.p. 123° (with loss of H_2O) or 185° (dried), and the *aminosulphonic acid* (**IV**), m.p. 142—143°, from citronellal. Solutions in air-free buffer of p_H 7·6 in N_2 show (liberation of SO_2) that no decomp. occurs with (**I**) or the corresponding Et compound at 37° or 50° for 1—4 days, that (**II**) shows 5% decomp. at 50° for 2 days, and (**III**) is decomposed at room temp. for 1 day. Taurine and aq. $NaHCO_3$–$ClCO_2CH_2Ph$ at room temp. afford *Na* N-*carbobenzyloxytaurine*, converted by PCl_5–C_6H_6, then NH_3, into the *amide*, m.p. 133°, and thence by H_2–Pd-black in aq. MeOH–AcOH into taurineamide hydrochloride, m.p. 133° (cf. Miller *et al.*, A., 1940, II, 339). A. T. P.

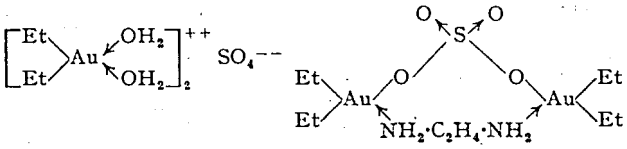
***tert.*-Amides of adipic, azelaic, and sebacic acids.** R. C. Fuson, J. W. Robinson, jun., and L. C. Behr (*J. Amer. Chem. Soc.*, 1941, **63**, 623—624).—*Adip-*, m.p. 52·5—53·5°, sol. in H_2O, sebac-, an oil (hydrochloride, m.p. ~0°; platinichloride, m.p. 148·5—150°, and *aurichloride*, m.p. 130—131°), and azela-tetraethyldiamide, an oil (hydrochloride, an oil; platinichloride, m.p. 140—142°, and *aurichloride*, m.p. 136·5—137°), and *sebactetramethyldiamide*, m.p. 87—88°, sol. in H_2O (hygroscopic hydrochloride, m.p. 122—126°; platinichloride, m.p. 156·5—158°, and *aurichloride*, m.p. 158—158·5°), are prepared from the diacid chloride and NHR_2. The solubilities and basicity are noted. R. S. C.

Aliphatic arsinic acids. III. Mono- and di-arsinomalonic acids. A. R. Marquez (*Anal. Asoc. Quím. Argentina*, 1940, **28**, 135—142).—$CHBr(CO_2Et)_2$ with As_2O_3 in excess of KOH yields only $CH_2(CO_2K)_2$ and K_3AsO_4 whereas $CBr_2(CO_2Et)_2$ gives *diarsinomalonic acid*, $C(AsO_3H_2)_2(CO_2Et)_2$, m.p. 128° (decomp.) (*Na_2*, *Ca*, and *Ba* salts). F. R. G.

Condensations by sodium. XX. Preparation and properties of organosodium compounds derived from butyl and propyl chlorides. A. A. Morton, G. M. Richardson, and A. T. Hallowell (*J. Amer. Chem. Soc.*, 1941, **63**, 327—330).—There is greater difficulty in effecting interaction of RCl with Na and poorer yields, greater tendency of disproportionation of NaR (judged by the relative amounts of mono- and di-carboxylic acids formed by CO_2), and greater resistance to C_6H_6 and PhMe in the order, R = Pr > Bu > amyl. NaBu can be conveniently prepared in PhMe. In PhMe at 69—75° PrCl and Na give 42% of PhBu, with *m*- and some *p*-C_6H_4PrBu, and unsaturated hydrocarbons including CHMe:CMeEt. R. S. C.

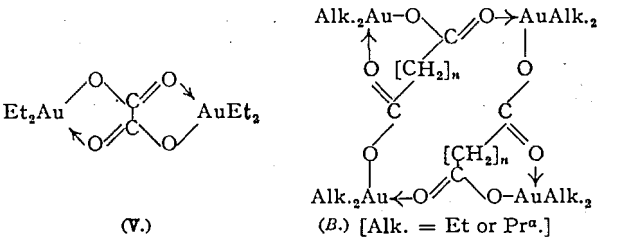
Reaction of ethylene oxide with Grignard's reagent. R. C. Huston and A. H. Agett (*J. Org. Chem.*, 1941, **6**, 123—133).—It is shown that the intermediate in the reaction between a Grignard reagent and $(CH_2)_2O$ is $C_4H_8O_2Br_2Mg$ (**I**) without an appreciable amount of $Br·[CH_2]_2·O·MgBr$ (**II**). Analytical results indicate the formation of (**I**) when $MgBr_2$ is treated with one or two mols. of $(CH_2)_2O$. Primary and *sec.* MgR_2 react with (**I**) only when heated or on long keeping to give $(R·[CH_2]_2·O)_2Mg$ (**III**) and with $(CH_2)_2O$ at room temp. to give (**III**). The absence of alcohol formation when MgRBr is treated at room temp. with one mol. of $(CH_2)_2O$ precludes the formation of appreciable amounts of (**II**). Bu*γ*, *tert.*-amyl, and *tert.*-hexyl Grignard reagents yield only $Br·[CH_2]_3·OH$ when treated with one or two mols. of $(CH_2)_2O$ as above. On long keeping Bu*γ* Grignard reagents give a small yield of *γγ*-dimethylbutan-α-ol (**IV**). $CH_2Ph·MgCl$ reacts readily with one or two mols. of $(CH_2)_2O$ at room temp. to give $Ph·[CH_2]_3·OH$. In this case the fundamental reaction is probably between $Mg(CH_2Ph)_2$ and $Mg([CH_2]_2·Cl)_2$ although a direct action of $CH_2Ph·MgCl$ and $(CH_2)_2O$ is a possibility. (**IV**) is oxidised by alkaline $KMnO_4$ to *ββ*-dimethylbutyric acid (**V**), converted through the chloride into the amide, m.p. 131°. (**V**) is also obtained by oxidising di*iso*butylene with CrO_3 to *ββ*-dimethylpentan-δ-one, which is further treated with Br and NaOH. *γδ*-Dimethylpentanol is identified by oxidation to *γδ*-dimethylvaleric acid (**VI**), which gives an amide, m.p. 95·5°, and an anilide, m.p. 67°; (**VI**) is also obtained from $CHMePr^{\beta}Br$ and $CH_2(CO_2Et)_2$. H. W.

Organic compounds of gold. VIII. Dialkyl gold derivatives of dibasic acids. C. S. Gibson and W. T. Weller. **IX. Structure of tetraethylsulphatodigold, $(Et_2Au)_4(SO_4)_2$.** R. V. G. Ewens and C. S. Gibson (*J.C.S.*, 1941, 102—108, 109—111; cf. A., 1939, II, 304).—VIII. Diethylmonobromogold (**I**) and Ag_2SO_4–$COMe_2$ afford *tetraethylsulphatodigold* (**II**), $(Et_4Au_2SO_4)_2$ (*A* in H_2O). Similarly prepared is the Pr^{α}_4 analogue (**III**), but the corresponding Bu^{α}_4 compound is unstable, and the Me_4 analogue could not be obtained; an aq. solution of (**II**) or (**III**) can be obtained from the ethylenediaminodialkylauric bromide and Ag_2SO_4. (**II**) and $(CH_2·NH_2)_2$–$COMe_2$ give *ethylenediaminotetraethylsulphatodigold* (**IV**), decomp. violently at ~147°; it is ionised in H_2O. *Ethylenediaminotetraethyldibromodigold*, decomp. with effervescence at ~113—114°, is



(*A*.) (**IV**.)

obtained from (**I**) (1 mol.) and ethylenediaminodiethylgold bromide (1·18 mols.) in ligroin–MeOH, or from equimols. of (**I**) and $(CH_2·NH_2)_2$ in ligroin–EtOH (cf. *loc. cit.*). (**II**) and 2 : 2'-dipyridyl yield 2 : 2'-*dipyridyltetraethylsulphatodigold*, m.p. 162—163° (decomp.), ionised in H_2O; the N atoms are attached to different Au atoms. Equimol. amounts of (**II**) and $Na_2C_2O_4$ in H_2O afford *tetraethyloxalatodigold* (**V**), m.p. 81°, decomp. explosively at ~120°; with excess of $Na_2C_2O_4$ and evaporation of the resulting aq. solution, *Na diethyloxalatodigold*, $C_6H_{10}O_4NaAu$, is formed [not obtainable from (**I**)]; its aq. solution and HBr yield (**I**). (**II**) and aq. $CH_2(CO_2Na)_2$ afford *tetraethylmalonatodigold* (*B*, *n* = 1; the valencies of the Au atoms are planar, but the mol. cannot be planar). Similarly prepared, in many cases using excess of the dibasic acid salt, are: *tetraethylmonomethylmalonatodigold*, m.p. 90—100°



(**V**.) (*B*.) [Alk. = Et or Pr^{α}.]

(decomp.), decomp. explosively at ~140°; *tetra*-n-*propylsuccinato*- (*B*, n = 2), m.p. 145—146° (decomp.), *-glutarato*- (*B*, *n* = 3), m.p. with decomp. from 90°, *-adipato*- (*B*, *n* = 4), m.p. ~124—132° (decomp.), *-pimelato*- (*B*, *n* = 5), m.p. 79—81°, decomp. ~100°, and *-suberato-digold* (*B*, *n* = 6), m.p. 86—88°, decomp. from ~110°. The mol. wt. of the unstable *tetraethylsaccharatodigold* could not be determined. *Tetraethyl-phthalato*-, $C_{16}H_{24}O_4Au_2$, decomp. without melting from ~120°, and *-3-nitrophthalato-digold* (mol. wt. not determined), *tetraethyl-*iso*phthalato*-, $C_{48}H_{72}O_{12}Au_8$, decomp. without melting, *-4-nitro*iso*phthalato*- (6Au), and *-terephthalato-digold* (mol. wt. not determined) are also prepared. Structural formulæ are discussed.

IX. The most probable structure of $(Et_2Au)_4(SO_4)_2$ is discussed and models are drawn. A. T. P.

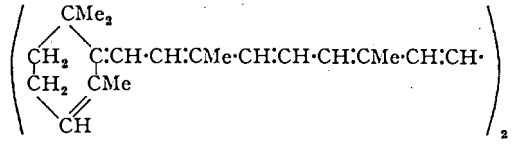
II.—HOMOCYCLIC.

Mechanism of catalytic hydrogenation of phenol [to hydrocarbons] under high pressures. VI. Comparison of two molybdenum catalysts. S. Andō (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 328—330B; cf. A., 1939, II, 146).—PhOH and *cyclo*hexane (**I**) are hydrogenated at 430° and 80—110 atm. for 1 hr. in presence of MoO_3 + S or MoS_2 on activated clay and reaction products are compared. The main fraction of oil from PhOH consists of C_6H_6, (**I**), and methyl*cyclo*pentane

(II). The saturated hydrocarbons from PhOH contain more (II) than those from (I). The amount of (II) from (I) is similar using either catalyst, whereas the amount of (II) from PhOH is much greater using MoS_2, and the quantity of high-boiling neutral oil formed is also larger. A. T. P.

Electrosynthesis of di*cyclo*hexyl. F. Fichter and A. Petrovitch (*Helv. Chim. Acta*, 1940, **23**, 806—808).—Electrolysis (Pt anode and cathode; 482 amp. per min.) of *cyclo*hexanecarboxylic acid (I) is KOH–MeOH–C_5H_5N affords a neutral oil, which is treated with KOH–MeOH to hydrolyse the *cyclo*hexyl ester of (I). Di*cyclo*hexyl ether is removed from unsaponifiable oil by HI (*d* 1·96)–AcOH, and the residue yields *cyclo*-hexanone and -hexanol, and di*cyclo*hexyl, m.p. 2·5—3°, b.p. 100–101°/10 mm. (14·2% yield). A. T. P.

Constitution of the so-called *iso*carotene. P. Karrer and G. Schwab (*Helv. Chim. Acta*, 1940, **23**, 578—581).—Analyses of *iso*carotene (I) (Kuhn *et al.*, A., 1932, 782) favour the formula of a dehydrocarotene. It is suggested from previous



(*A*.)

work (*ibid.*, 1256) that (I) is actually (*A*), *i.e.*, dehydro-β-carotene, formation of which from β-carotene tetraiodide involves loss of 2I and 2HI. H. B.

Catalytic transformations of ethylbenzene. S. R. Sergienko (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 36—40; cf. A., 1940, II, 248).—The optimum temp. for smooth catalytic dehydrogenation of PhEt to styrene (I) is below 600°. At ~600° C_6H_6 and PhMe are formed and at higher temp. the ring is decomposed. With $ZnCrO_4$ as a catalyst at 500° to 600°, the yield of (I) increases from 10 to 35%. Addition of ZnO or Cr_2O_3 to the catalyst increases the yield of PhMe and of C_6H_6 and PhMe respectively. (I) is determined from the Br val. of the mixtures. F. R. G.

Hydrogen fluoride as a condensing agent. XIII. Sulphonation. J. H. Simons, H. J. Passino, and S. Archer (*J. Amer. Chem. Soc.*, 1941, **63**, 608—609; cf. A., 1940, II, 301).—C_6H_6, HF, and H_2SO_4 at 85—95° give 75% of $PhSO_3H$ and a trace of Ph_2SO_2; at 140—150° 40% of Ph_2SO_2 is obtained. FSO_3H with C_6H_6 at 160° gives 14% of Ph_2SO_2 and at 60—70° gives 53% of $PhSO_3H$. H_2SO_4 + HF probably reacts as FSO_3H. *p*-$C_6H_4Me{\cdot}SO_3H$, C_6H_6, and HF at 85—95° give a little *p*-$C_6H_4Me{\cdot}SO_2{\cdot}Ph$, obtained similarly from $PhSO_3H$ and PhMe. C_6H_6, HNO_3, and HF at 0° give 83% of $PhNO_2$, but no $C_6H_4(NO_2)_2$. R. S. C.

α-Chloro-α-sulphonyl-amides. E. Barr, W. M. Ziegler, and R. Connor (*J. Amer. Chem. Soc.*, 1941, **63**, 105—107; cf. A., 1941, II, 2).—The equiv. amount of Cl_2 in AcOH converts the Cl-free amides into *α-chloro-α-p-toluenesulphonyl-acetamide* (I), m.p. 169—171°, and -n-*butyramide*, m.p. 58—60°, *α-chloro-α-n-butanesulphonyl-propionamide*, *m.p.* 65—66°, and -n-*butyramide*, m.p. 58—59°, *αα-dichloro*-p-*toluene*- (II), m.p. 131—133°), and -α-n-*butane-sulphonylacetamide*, m.p. 89—90°. The Cl-amides are more reactive then are the Br-amides (*loc. cit.*), sometimes losing Cl in warm H_2O or aq. EtOH; they react normally with N_2H_4, HI, piperidine, and RSH. Repeated recrystallisation of (II) from aq. EtOH gives first (I) and then (from H_2O) *p*-$C_6H_4Me{\cdot}SO_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ (III). $CHCl_2{\cdot}CO{\cdot}NH_2$ (1·5) with RSNa (1 mol.) (R = Bu$^\alpha$ or *p*-C_6H_4Me) in EtOH at room temp. gives $(SR)_2CH{\cdot}CO{\cdot}NH_2$. (III) reacts slowly, if at all, with Bu$^\gamma$OCl in CCl_4. *p*-$C_6H_4Me{\cdot}SO_2{\cdot}CHNa{\cdot}CO{\cdot}NH_2$ and *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_6H_6, first at room temp. and then at the b.p., give *p*-$C_6H_4Me{\cdot}SO_2{\cdot}CHCl_2$ (21%) and (*p*-$C_6H_4Me{\cdot}SO_2)_2$ (6%). M.p. are corr. R. S. C.

Synthesis of substituted stilbenes and diphenylbutadienes. F. Bergmann and (Miss) Z. Weinberg (*J. Org. Chem.*, 1941, **6**, 134—139).—Condensation of 1-$C_{10}H_7{\cdot}CHO$ with *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ by piperidine at 160° gives a 13% yield of *α-p-nitrophenyl-β-1-naphthylethylene* (I), m.p. 183° (*dibromide*, m.p. 183°), whereas by use of PbO and Ac_2O at 140° a 20% yield of (I) is obtained with a 25% yield of *α-p-nitrophenyl-β-1-naphthylacrylic acid* (II), m.p. 201°; (II) does not add Br but is converted by CH_2N_2 into the *Me* ester, m.p. 140°. (I) is unchanged by $SnCl_2$ in AcOH or Fe dust and HCl in EtOH but is reduced by $FeSO_4$ and conc. NH_3 in boiling aq. EtOH to *α-p-aminophenyl-β-1-naphthylethylene*, m.p. 114°. *α-p*-Aminophenyl-*β*-1-naphthylacrylic acid, from (II), $FeSO_4$, and NH_3, gives a *hydrochloride*, m.p. 254°. *α-Phenyl-β-4-nitronaphthylethylene*, m.p. 94°, obtained by the diazo coupling of $CHPh{:}CH{\cdot}CO_2H$ and 4 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$, is shown to have the *trans*-structure by the stability of its *dibromide*, m.p. 182°, which is unchanged by boiling C_5H_5N. Diazo-coupling of *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ and cinnamylideneacrylic acid in $COMe_2$ gives *δ-phenyl-α-p-nitrophenyl-Δ$^{\alpha\gamma}$-butadiene* (III), m.p. 171—172°, also obtained with *δ-phenyl-α-p-nitrophenyl-Δ$^{\alpha\gamma}$-pentadienoic acid* (IV), m.p. 256°, from *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$, $CHPh{:}CH{\cdot}CHO$, and PbO in boiling Ac_2O. (III) and maleic anhydride at 100° and then at 110° give the *anhydride*, $C_{20}H_{15}O_3N$, m.p. 213°. (III) with excess of Br in CCl_4 yields a *tetrabromide*, m.p. 245—246°. $FeSO_4$ and NH_3 reduce (III) to *δ-phenyl-α-p-aminophenyl-Δ$^{\alpha\gamma}$-butadiene*, m.p. 167° (*trichloroacetyl* derivative, m.p. 177—178°), (IV) does not add Br but its *Me* ester, m.p. 134°, gives a *dibromide*, m.p. 248—249°. *δ-Phenyl-α-p-aminophenyl-Δ$^{\alpha\gamma}$-pentadienoic acid* has m.p. 258°. H. W.

***spirocyclo*Hexane-1 : 1′-indane, its synthesis and properties.** M. Levitz, D. Perlman, and M. T. Bogert (*J. Org. Chem.*, 1941, **6**, 105—119).—*spirocyclo*Hexane-1 : 1′-tetrahydronaphthalene is oxidised by CrO_3 in AcOH at 20—25° and then at room temp. to 4′-*keto*spirocyclo*hexane*-1 : 1′-*tetrahydronaphthalene* (I), b.p. 147—150°/1 mm., m.p. 63·5—64° (*semicarbazone*, m.p. 236·5—237°; *oxime*, m.p. 178—178·5°), with a small proportion of the 3′ : 4′-*diketone*, m.p. 131·5—132·5°, the constitution of which is established by its oxidation (H_2O_2 in alkaline solution) to *αα*-pentamethylenehomophthalic acid (II), m.p. 154—155°, and by its conversion by *o*-$C_6H_4(NH_2)_2$ in EtOH into the *quinoxaline* derivative, $C_{21}H_{20}N_2$, m.p. 142·5—143·5°. (I) in EtOH–Et_2O is transformed by $BuNO_2$ and HCl into 3′-*oximino*-4′-*keto*spirocyclo*hexane*-1 : 1′-*tetrahydronaphthalene*, m.p. 203·5—204·5° (decomp.), converted by a Beckmann rearrangement of the second order (*p*-$C_6H_4Me{\cdot}SO_2Cl$ and 10% NaOH) into 1-o-*carboxyphenyl*cyclo*hexylacetonitrile*, m.p. 147·5—148·5°, slowly hydrolysed by boiling 10% NaOH to 1-o-*carboxyphenyl*cyclo*hexylacetic acid*, m.p. 206—207°. This acid is cyclised by Ac_2O to spirocyclo*hexane*-1 : 1′-*indan*-3′-*one* (III), b.p. 128—129°/2 mm. [NO_2-derivative, m.p. 192—192·5°; *semicarbazone*, m.p. 211·5—212·5°; *oxime*, m.p. 137—138° (IV), and its NO_2-derivative, m.p. 187—188°]. Clemmensen reduction of (IV) leads to spirocyclo*hexane*-1 : 1′-*indane* (V), b.p. 99—100°/2 mm., 132—133°/10 mm., which when oxidised affords (II). It is acetylated in $PhNO_2$ or, preferably, in light petroleum to *acetyl*spirocyclo*hexane*-1 : 1′-*indane*, m.p. 97—97·5° (*semicarbazone*, m.p. 231—231·5°), which is oxidised by NaOCl to spirocyclo*hexane*-1 : 1′-*indanecarboxylic acid*, m.p. 239—240°. In repetition of the work of Cook *et al.* (A., 1939, II, 103) the cyclisation of 1-*β*-phenylethyl*cyclo*hexan-1-ol (VI) and oximation of the mixtures of ketones produced by oxidation gives three oximes, m.p. 187—188° (identical with that of m.p. 187·5° reported by Cook), 136·5—137° [identical with (IV)], and m.p. 123—124° (identical with that of m.p. 124° reported by Cook); an oxime, m.p. 175—177°, could not be detected. The first synthetic proof is thus afforded that (V) is obtained by the cyclisation of (VI). It seems probable that the substance separated by van der Kamp and Mosettig (A., 1930, 1438) from the cyclisation products of (VI) was mainly (V) and not *trans*-octahydrophenanthrene. Aromatic products are not obtained when (V) is heated with Se for 44 hr. at 300—340° or with S for 40 hr. at 300°. Heating with Pd–C at 330—340° for 15 hr. gives a small proportion of phenanthrene (VII). Vapour-phase dehydrogenation at 370—375° gives considerable amounts of (VII) whereas at 400—420° the main product is anthracene. H. W.

Reactivity of the naphthalene ring in relation to the dispersal of electromeric effects. Methyl and chloromethyl groups. V. A. Izmailski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 98—102).—The polarising influence of Me and CH_2Cl is discussed. Differences in reactivity of substituted C_6H_6, $C_{10}H_8$, and anthracene rings are explained in terms of dispersal of electromeric effects. A. Lr.

Synthesis of 1-methyl-6-*iso*propylphenanthrene. S. N. Slater (*J.C.S.*, 1941, 68—70).—*p*-$C_6H_4Pr^\beta{\cdot}CH_2{\cdot}CO_2Et$ and Na–EtOH at 180°, then 160° to 100°, give *p*-$C_6H_4Pr^\beta{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ and thence homocuminyl bromide.

The Grignard reagent from the latter and 2 : 6-dimethyl-*cyclo*hexanone afford 2 : 6-*dimethyl*-1-β-p-*cuminylethyl*cyclo*hexanol*, b.p. 164—172°/0·5 mm., and thence (H_2SO_4–H_2O at room temp.) 1 : 12-*dimethyl*-6-iso*propyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*, b.p. 180—190°/12 mm., which with Se at 300°, then 340°, gives 1-*methyl*-6-iso*propylphenanthrene* (I), m.p. 45—46° (CrO_3–AcOH give the *quinone*, m.p. 144—146°), purified through the *picrate*, m.p. 143°. (I) is not identical with the hydrocarbon obtained by dehydrogenation of the diterpene rimuene (confirms results of Brandt, A., 1938, II, 500). A. T. P.

Aromatic cyclodehydration. IX. 9-Alkylphenanthrenes. C. K. Bradsher and S. T. Amore (*J. Amer. Chem. Soc.*, 1941, **63**, 493—495; cf. A., 1941, II, 8).—*o*-C_6H_4Ph·CO·CH_2·OMe and MgRHal in boiling Et_2O give crude carbinols, which in boiling 40% aq. HBr–AcOH give 9-ethyl- (I) (53%), m.p. 62—63° (picrate, m.p. 123—124°), 9-*n*-propyl- (II) (51%), m.p. 57·5—58° (picrate, m.p. 98—99°), 9-*n*-butyl- (III) (40%), m.p. 80—81°, and 9-benzyl-phenanthrene, m.p. 152·5—153°. $MgPr^{\beta}Br$ gives only phenanthrene. Mg 2-diphenylyl iodide and RCHO in boiling (?) Et_2O give carbinols, dehydrated by $KHSO_4$ at 160° to olefines (and a little Ph_2), which with *o*-CO_2H·C_6H_4·CO_3H (2—3 mols.) give oxides and thence by boiling 40% aq. HBr–AcOH (I) (41%, here and below calc. from the RCHO used), (II) (26%), (III) (21%), 9-iso*propyl*- (28%), m.p. 41—42 (picrate, m.p. 109—110°), and 9-n-*amyl*-*phenanthrene* (25%), m.p. 69—70°. Data of Miller *et al.* (cf. A., 1935, 741) are erroneous. R. S. C.

9-*n*-Propyl- and 9-*n*-butyl-phenanthrene. G. B. Bachmann and R. I. Hoaglin (*J. Amer. Chem. Soc.*, 1941, **63**, 621).—The data of Bradsher and Amore (preceding abstract) are confirmed (cf. Miller *et al.*, A., 1935, 741). R. S. C.

Synthesis of 10-methyl-3′-*iso*propyl-1 : 2-benzanthracene from 9 : 10-dihydroretene. L. F. Fieser and R. C. Clapp (*J. Amer. Chem. Soc.*, 1941, **63**, 319—323).—9 : 10-Dihydroretene (prep. in 86% yield by H_2–Cu chromite at 160°/1250 lb.), $(CH_3·CO)_2O$, and $AlCl_3$ in $PhNO_2$ at 0°, later ~25°, give *γ-keto*-γ-9 : 10-*dihydro*-2-*retyl*-n-*butyric acid* (I) (80%), m.p. 159·2—160° (decomp.), the Na salt of which with H_2–Cu chromite in 10% NaOH at 195—200°/3000 lb. (less well by Clemmensen–Martin reduction) gives 69% of γ-9 : 10-*dihydro*-2-*retyl*-n-*butyric acid* (II), m.p. 161·8—162·8°, cyclised in HF at room temp. to 8-*keto*-10-*methyl*-3′-iso*propyl*-3 : 4 : 5 : 6 : 7 : 8-*hexahydro*-1 : 2-*benzanthracene* (III), m.p. 133·8—134·8°. With H_2–Cu in abs. EtOH at 160°, (III) gives 10-*methyl*-3′-iso*propyl*-3 : 4 : 5 : 6 : 7 : 8-*hexahydro*-1 : 2-*benzanthracene* (51%), m.p. 44·8—46°, dehydrogenated by Pd–C–N_2 at, successively, 220°, 265—275°, and 295—300° to 10-*methyl*-3′-iso*propyl*-1 : 2-*benzanthracene* (IV), colourless, m.p. 98—99° [picrate, m.p. 143·8—144·5°; *s*-$C_6H_3(NO_2)_3$ compound, m.p. 155·8—156·5°]. The structure of (IV) is proved by its absorption spectra. Coupled with oxidation of (I) by HNO_3 at 190—200° to 1 : 2 : 3 : 4-$C_6H_2(CO_2H)_4$, this in turn proves the orientation of the intermediates. The structure of Adelson and Bogert's intermediates (A., 1937, II, 503), including *γ-keto*-γ-3-*retylbutyric acid* (21% yield), m.p. 198—199·5° (decomp.), and 5-*keto*-10-*methyl*-3′-iso*propyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 139·3—140·3° (by-product, m.p. 132—133·5°), the synthesis of which is modified, believed by them to be the 6-isomerides, is decided by the identity of their "5 : 6-benzoretene" with (IV) and the non-identity of the intermediates from the 2-retyl compounds described below. The *Me* ester, m.p. 80·5—81·8°, of (I) with Br in $CHCl_3$ at 0° gives the *β-Br*-ester, m.p. 89·5—90·5°, converted by NaOAc at 100° into *Me γ-keto*-γ-9 : 10-*dihydro*-2-*retyl*-Δ^{α}-*butenoate* (V), m.p. 105—106·3°, but by NaOH in aq. EtOH into a 9 : 10-*dihydroretenecarboxylic acid*, m.p. 199—200·5°, which is similarly obtained from (V). Over Pd–C–N_2 at 220°, later 265°, (I) gives 28% of *γ-keto*-γ-2-*retyl*-n-*butyric acid*, m.p. 188·5—190° (decomp.); the *Me* ester, m.p. 55·5—56·5°, of (II) gives similarly *Me* γ-2-*retyl*-n-*butyrate* (60%), m.p. 81—81·8°, and thence the *acid*, m.p. 197·8—198·6°. M.p. are corr. R. S. C.

Synthesis of 7 : 9 : 10- and 8 : 9 : 10-trimethyl-1 : 2-benzanthracene. W. E. Bachmann and J. M. Chemerda (*J. Org. Chem.*, 1941, **6**, 36—49).—Reduction of 6-acetylphenanthrene by $Al(OPr^{\beta})_3$ in boiling $Pr^{\beta}OH$ affords 6-*phenanthrylmethylcarbinol*, m.p. 79—81°; the corresponding *bromide*, m.p. 87—89°, is transformed by $CHNa(CO_2Et)_2$ followed by hydrolysis and decarboxylation into β-6-phenanthrylbutyric acid, m.p. 104—106°. This is converted by $SOCl_2$ in boiling Et_2O (or in Et_2O containing C_5H_5N at room temp.) into the chloride and thence by CH_2N_2 followed by hydrolysis and acidification into *γ-6-phenanthrylvaleric acid* (I), m.p. 75—77°; alternatively the diazo-ketone is transformed by dry Ag_2O and NH_3 in MeOH into *γ-6-phenanthrylvaleramide*, m.p. 138—139°, which is hydrolysed by 10% NaOH to (I). PCl_5 in dry C_6H_6 transforms (I) into the chloride, cyclised by $SnCl_4$ to 5-*keto*-8-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 130—131·5°, reduced [$Al(OPr^{\beta})_3$ in $Pr^{\beta}OH$] and then dehydrated (Pd–C at 230—250° and then at 300—310°) to 8-methyl-1 : 2-benzanthracene (II), m.p. 117—117·5°, remelting at the same temp. Alternatively, 8-keto-3 : 4 : 5 : 6 : 7 : 8-hexahydro-1 : 2-benzanthracene is converted by MgMeI into 8-*hydroxy*-8-*methyl*-3 : 4 : 5 : 6 : 7 : 8-*hexahydro*-1 : 2-*benzanthracene*, m.p. 115·5—117°, which is dehydrated and dehydrogenated (Pd–C at 300—320°) to (II). Oxidation of (II), best by $Na_2Cr_2O_7$, in boiling $EtCO_2H$ yields 8-*methyl*-1 : 2-*benzanthraquinone*, m.p. 192—194°, transformed by MgMeI into the corresponding diol, analysed as the *Me*$_2$ *ether*, m.p. 205—210° in bath preheated to 180°, which is converted by Na in C_6H_6–Et_2O followed by MeOH and HCl into 8 : 9 : 10-*trimethyl*-1 : 2-*benzanthracene*, m.p. 102—103·5° (*picrate*, m.p. 116—117°). Improved directions are given for condensing 6-α-bromopropionylphenanthrene with $CHNa(CO_2Et)_2$ and subsequent hydrolysis and decarboxylation to β-6-phenanthrylbutyric acid, m.p. 144—145°, remelting at 155—156°, which is reduced (Zn–Hg–AcOH–HCl–PhMe) to γ-6-phenanthryl-β-methylbutyric acid, m.p. 99—101°. The corresponding chloride is cyclised ($SnCl_4$) to 5-*keto*-7-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 133·5—134°, reduced (Clemmensen) to 7-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 114—115·5°, and by $Al(OPr^{\beta})_3$ to 5-*hydroxy*-7-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*, m.p. 145—146°. Treatment of either of these compounds by Pd–C at 300—320° affords 7-methyl-1 : 2-benzanthracene, m.p. 179—181°, also obtained from 8-keto-7-methyl-3 : 4 : 5 : 6 : 7 : 8-hexahydro-1 : 2-benzanthracene (III). It is converted by oxidation followed by treatment with MgMeI and then with MeOH–C_6H_6–H_2SO_4 into 9 : 10-*dimethoxy*-7 : 9 : 10-*trimethyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene*, m.p. 198—201°, and thence into 7 : 9 : 10-*trimethyl*-1 : 2-*benzanthracene*, m.p. 99·5—100° (*picrate*, m.p. 139—140° in a Pyrex tube). 5-Keto-8-methyl-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene is converted by MgMeI followed by Pd–C at 310—320° into 5 : 8-dimethyl-1 : 2-benzanthracene, m.p. 133·5—134·5° (picrate, m.p. 173—173·5°). Analogously, 5-keto-7-methyl-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene affords 5 : 7-*dimethyl*-1 : 2-*benzanthracene*, m.p. 123·5—124·5°, and then 124—125° (*picrate*, m.p. 186·5—187·5° in a Pyrex tube). 8-Keto-3 : 4 : 5 : 6 : 7 : 8-hexahydro-1 : 2-benzanthracene is condensed by NaOMe with $Me_2C_2O_4$ to *Me* 8-*keto*-3 : 4 : 5 : 6 : 7 : 8-*hexahydro*-1 : 2-*benzanthracene*-7-*glyoxylate*, m.p. 133° and then 133—134° after softening at 128°, which gives *Me* 8-*keto*-3 : 4 : 5 : 6 : 7 : 8-*hexahydro*-1 : 2-*benzanthracene*-7-*carboxylate*, m.p. 110—125°. This is converted by NaOMe–MeI in MeOH–C_6H_6 into *Me* 8-*keto*-7-*methyl*-3 : 4 : 5 : 6 : 7 : 8-*hexahydro*-1 : 2-*benzanthracene*-7-*carboxylate*, m.p. 109—111°, transformed by boiling HCl–AcOH into (III), m.p. 105·5—106°. Analogously, *Me* 5-*keto*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*-6-*glyoxylate*, m.p. 162—163° (decomp.), gives successively *Me* 5-*keto*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*-6-*carboxylate*, m.p. 158—159·5°, *Me* 5-*keto*-6-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*-6-*carboxylate*, m.p. 115—116°, and 5-keto-6-methyl-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene, m.p. 137—138°; this ketone is reduced by $Al(OPr^{\beta})_3$ and dehydrogenated by Pd–C to 6-methyl-1 : 2-benzanthracene, m.p. 149—151·5° (picrate, m.p. 157—158°), and converted by MgMeI followed by dehydrogenation into 5 : 6-dimethyl-1 : 2-benzanthracene, m.p. 187—188° (picrate, m.p. 192—193°). H. W.

Synthesis of 4- and 5-methylcholanthrene. W. E. Bachmann and J. M. Chemerda (*J. Org. Chem.*, 1941, **6**, 50—53).—5-Keto-7-methyl-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene is reduced [$Al(OPr^{\beta})_3$] to the corresponding *sec.* alcohol, which is converted (HCl) into the chloride. This is transformed by $CH_2(CO_2Et)_2$ into 7-methyl-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene-7-acetic acid, the chloride of which is cyclised ($SnCl_4$) to 1-keto-4-methylcholanthrene; this is reduced (Clemmensen) and dehydrogenated (Pd–C) to 4-methylcholanthrene, m.p. 154—155° (picrate, m.p. 172—173°). Simi-

larly 5-keto-8-methyl-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene is transformed into *5-methylcholanthrene*, m.p. (vac.) 160—161·5° and then 164—165° (*picrate*, m.p. 192—193° in a Pyrex tube). The intermediates are probably mixtures of stereoisomerides due to the presence of two asymmetric C in the reduced ring. H. W.

Comparisons of the intensity of fluorescence of cholanthrene and its homologues.—See A., 1941, I, 98.

Fluorinated amines of the pressor type. C. M. Suter and A. W. Weston (*J. Amer. Chem. Soc.*, 1941, **63**, 602—605).—PhF, Br, and Fe filings give mainly *p*-C_6H_4BrF, b.p. 153—161°, with less 2 : 4-*dibromofluorobenzene*, b.p. 215·4—216°/745 mm., 102—103°/23 mm. (also obtained in 24% yield from 2 : 4 : 1-$C_6H_3Br_2{\cdot}NH_2$ by pyrolysis of the derived diazonium borofluoride, decomp. 182°), and a little (?) 3 : 4 : 1-$C_6H_3Br_2F$, m.p. 66·5—67°. $(CH_2)_2O$ and *p*-$C_6H_4F{\cdot}MgBr$ (I) in C_6H_6–Et_2O at <10° and later 45° give *p*-$C_6H_4F{\cdot}[CH_2]_2{\cdot}OH$, b.p. 117—118°/20 mm. [benzoate, m.p. 54·5—55·5° (lit. 43—44°)], converted by PBr_3 in C_6H_6 into the *bromide*, b.p. 101—102°/17 mm., which with NH_3–EtOH at room temp. gives *β-p-fluorophenylethylamine*, b.p. 99—100°/24 mm. (*hydrochloride*, m.p. 206—208°), and with NH_2Me in Bu^{a}OH at 100° gives *β-p-fluorophenylethylmethylamine* (II), b.p. 105—107°/26 mm. (*hydrochloride*, m.p. 163—164°). *p*-$C_6H_4F{\cdot}CH_2Cl$ and NaCN in boiling EtOH give p-*fluorobenzyl cyanide*, b.p. 122—123°/21 mm., which resisted reduction (Na, EtOH). (I) with $CH_2Cl{\cdot}COMe$ in boiling Et_2O gives *p*-$C_6H_4F{\cdot}CH_2{\cdot}COMe$, b.p. 106—107°/18 mm. (*semicarbazone*, m.p. 200·5—201·5°), which with $HCO{\cdot}NH_2$ at the b.p. gives an amide, converted by boiling 30% NaOH into *β-p-fluorophenylisopropylamine*, b.p. 95—96°/17 mm. (carbonate; *hydrochloride*, m.p. 156—157°). Of these bases, (II) is the most promising as a pressor substance. M.p. are corr. R. S. C.

Nuclear iodination of aromatic amines. W. Militzer, E. Smith, and E. Evans (*J. Amer. Chem. Soc.*, 1941, **63**, 436).—NH_2Ar, AcOH (1 equiv.), and I in H_2O give *p*-$C_6H_4I{\cdot}NH_2$ (30—40% at 15°), m.p. 63° (purified as H sulphate), 2 : 4 : 1-$C_6H_3I_2{\cdot}NH_2$ (small yield at 70—80°), m.p. 95°, *5-iodo-2-aminobenzoic acid* (50% at 15°), m.p. 210° (purified as NH_4 salt), *p*-$C_6H_4I{\cdot}NMe_2$ (very small yield at 15°), m.p. 80°, and 1 : 5 : 2-$C_6H_3MeI{\cdot}NH_2$ (40—45% at 15°), m.p. 86—88°, but *p*-$NH_2{\cdot}C_6H_4{\cdot}COMe$, *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, and NHPhAc do not react. *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ and I in AcOH at 80—90° give *3-iodo-4-aminobenzenesulphonamide* (20—25%), m.p. 182°. R. S. C.

Hydrogen exchange reactions of aromatic *tert.* amines. W. G. Brown and N. J. Letang (*J. Amer. Chem. Soc.*, 1941, **63**, 358—361).—The acid-catalysed H-exchange of α-$C_{10}H_7{\cdot}NMe_2$ is greatly retarded by 8-Cl or 8-NO_2 and 1 : 8-exchanges more slowly than 1 : 5-$C_{10}H_6(NMe_2)_2$; these differences are ascribed to steric causes (A., 1939, I, 617). The reaction proceeds less readily with carbazole or acridane than with $NHPh_2$ derivatives. 10-Methylacridane undergoes also a base-catalysed exchange, probably involving the CH_2. *o*-$C_6H_4(CO)_2N{\cdot}C_{10}H_7$-α gives 8 : 1-$NO_2{\cdot}C_{10}H_6{\cdot}NH_2$ and thence (Me_2SO_4) *8-nitro-1-naphthyldimethylamine*, m.p. 75°. 8 : 1-$C_{10}H_6Cl{\cdot}NH_2$ (prep. from 8 : 1-$C_{10}H_6Cl{\cdot}NO_2$ by $SnCl_2$–HCl), m.p. 88—89°, with Me_2SO_4 gives *8-chloro-1-naphthyldimethylamine*, b.p. 111—112°/4 mm. 1 : 8- and 1 : 5-$C_{10}H_6(NO_2)_2$ give similarly 1 : 8-, b.p. 144—145°/4 mm., and 1 : 5-*bisdimethylaminonaphthalene*, m.p. 90·5°, respectively. R. S. C.

Carbimides of 3 : 4-benzpyrene and 10-methyl-1 : 2-benzanthracene. H. J. Creech (*J. Amer. Chem. Soc.*, 1941, **63**, 576—578).—5-Nitro-3 : 4-benzpyrene (modified prep.), m.p. 254·5—255·5°, and $SnCl_2$–HCl–AcOH give the 5-NH_2-derivative, m.p. 239—241° (decomp.), 246·5—247·5° (vac.), and thence by $COCl_2$ in boiling C_6H_6–PhMe the *carbimide*, m.p. 183·5—184°, which is converted by NH_3 in aq. dioxan into the *carbamide*, m.p. ~370° (decomp. from 300°; vac.), by boiling abs. EtOH into *Et* 3 : 4-*benzpyrenyl-5-carbamate*, m.p. 249—249·5°, by $NH_2{\cdot}[CH_2]_2{\cdot}OH$ into *β*-3 : 4-*benzpyrenyl-5-carbamidoethanol*, m.p. ~310° (decomp. from 290°; vac.), and by $NH_2{\cdot}CH_2{\cdot}CO_2H$ in aq. Na_2CO_3–$NaHCO_3$ into 3 : 4-*benzpyrenyl-5-carbamidoacetic acid*, m.p. ~320° (decomp.) [*Et* ester, m.p. 265—330° (decomp.)]. *3-Amino-10-methyl-1 : 2-benzanthracene* (prep. from the 3-OH-compound by NH_3–$NaHSO_3$–H_2O–dioxan at 175—185°), m.p. 189—189·5° (vac.), 188—189° (air), gives *10-methyl-1 : 2-benzanthryl-3-carbimide*, m.p. 149·5—150°, and *-3-carbamide*, m.p. 348—350° (vac.), *Et* *10-methyl-1 : 2-benzanthryl-3-carbamate*, m.p. 201—201·5°, and *-3-carbamidoacetate*, m.p. 213—214° (vac.). M.p. are corr. R. S. C.

Phosphoric acid derivatives of sulphanilamides.—See B., 1941, III, 78.

Relationships between respiratory activities of bacteria and their sensitiveness to sulphanilamide, *p*-hydroxylamino- and *p*-nitro-benzenesulphonamide. H. Burton, J. W. McLeod, T. S. McLeod, and A. Mayr-Harting (*Brit. J. exp. Path.*, 1940, **21**, 288—302; see also A., 1941, III, 139).—*p*-$NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ is reduced (Zn dust, boiling aq. EtOH–NH_4Cl) to p-*hydroxylaminobenzenesulphonamide*, m.p. 163—164° (decomp.), which reduces cold aq. NH_3–$AgNO_3$. 2-p-*Nitrobenzenesulphonamidopyridine*, decomp. 175° [from *p*-$NO_2{\cdot}C_6H_4{\cdot}SO_2Cl$ and 2-aminopyridine in C_5H_5N at 100° (bath)], similarly gives some impure 2-p-*hydroxylaminobenzenesulphonamidopyridine*, m.p. 147° (decomp.; previous softening), together with amorphous orange-red material. H. B.

***p*-Aminobenzenesulphonhydroxyl-amides and -alkylamides.**—See B., 1941, III, 108.

4-Aminodiphenyl-4′-sulphonamide and its derivatives. I. F. Halverstadt and W. D. Kumler (*J. Amer. Chem. Soc.*, 1941, **63**, 624—625).—4-NHAc·$C_6H_4{\cdot}C_6H_4{\cdot}SO_2Cl$-4′, decomp. after sintering at 180°, and thence 4-acetamido-, m.p. 295—296·5° (decomp.), and 4-amino-diphenyl-4′-sulphonamide, m.p. 259—260° and 266—267° (decomp.) (also obtained from the NO_2-amide, m.p. 225·5—227°), are prepared. M.p. are corr. R. S. C.

Electrolytic preparation of benzidine-3 : 3′-disulphonic acid. L. M. Grubina and V. V. Stender (*J. Appl. Chem. Russ.*, 1940, **13**, 1028—1039).—Benzidine-3 : 3′-disulphonic acid (I) is prepared electrolytically from *m*-$NO_2{\cdot}C_6H_4{\cdot}SO_3Na$ (II) by a two-stage process: (i) cathodic reduction to azo- and azoxy-compounds, in alkaline solution, (ii) further reduction to hydrazo-compound, with simultaneous rearrangement to (I), in acid solution. Optimum conditions are: (i) initial c.d. 5, final c.d. 2 amp. per sq. dm., concn. of (II) 15—20%, p_H of catholyte slightly >7, temp. immaterial (0—100°), cathode Ni or Fe, anolyte 10% Na_2SO_4, (ii) c.d. 0·5—1 amp. per sq. dm., temp. immaterial, p_H of catholyte slightly <7, cathode Pb, anolyte 10% Na_2SO_4. In both stages the yield falls with rising c.d. Increase in p_H does not affect the yield in stage (i); in stage (ii) it falls rapidly as the [H_2SO_4] exceeds 20%. Addition of KI, $CO(NH_2)_2$, or H_3BO_3 does not affect the process. The yield of pure (I) is 55—60% (on current). R. T.

Kinetics and mechanisms of the coupling of diazonium salts with aromatic amines in buffer solutions. R. Wistar and P. D. Bartlett (*J. Amer. Chem. Soc.*, 1941, **63**, 413—417).—The effect of p_H on the rate of coupling of 1 : 4-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ with *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$ and of 1 : 8-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3H$ with PhN_2Cl in buffered aq. solution at 25°, Conant and Peterson's data (A., 1930, 711) on coupling with phenols, and current electronic views prove that reaction occurs between the diazonium cation and the free amine or phenoxide ion. R. S. C.

Condensations. XV. Electronic mechanism of the diazo-coupling reaction. C. R. Hauser and D. S. Breslow (*J. Amer. Chem. Soc.*, 1941, **63**, 418—420; cf. A., 1941, II, 4).—PhN_2Cl couples with *β*-$C_{10}H_7{\cdot}OH$ or *β*-$C_{10}H_7{\cdot}ONa$ in anhyd. C_5H_5N. Benzenediazodiperidide, $NPh{:}N{\cdot}N{<}(CH_2)_5$ (I) couples similarly in anhyd. C_5H_5N if $C_5H_5NH^+$ (*e.g.*, from the chloride) is also present; weaker proton donors ($NHEt_3^+$, *β*-$C_{10}H_7{\cdot}OH$) do not decompose (I) to PhN_2^+ and thus do not cause coupling. These facts and electronic considerations indicate that $Ar{\cdot}N{:}N^+$ (and its resonance isomeride, $Ar{\cdot}\overset{+}{N}{:}N$), and not $Ar{\cdot}N{:}N{\cdot}OH$, is the effective reagent. R. S. C.

Binding between molecules and intramolecular complexes of certain phenols, and the dispersion of absorption bands.—See A., 1940, I, 148.

Preparation of nitrosophenols from benzene or other aromatic hydrocarbons at room temperature. O. Baudisch (*J. Amer. Chem. Soc.*, 1940, **63**, 622).—Addition of NH_2OH,HCl and then of H_2O_2 to 2% aq. $Na_3[Fe(CN)_5NH_3]$ (I) and C_6H_6–ligroin gives *o*-$OH{\cdot}C_6H_4{\cdot}NO$, isolated as Cu salt. Similar results (variable yields) are obtained with PhMe, PhEt, xylene, $CPh{:}CH$, PhCl, or PhBr. Ionised Fe$^{\cdot\cdot}$ salts cannot replace (I). Reactions proceed by means of a short-lived NOH radical, "trapped" by the subsidiary linking of the

Fe in $Na_3[Fe(CN)_5H_2O]$ [which arises from (I)] (cf. A., 1941, II, 39). R. S. C.

Condensation of diphenylalkylcarbinols with phenol in presence of aluminium chloride. R. C. Huston and R. I. Jackson (*J. Amer. Chem. Soc.*, 1941, **63**, 541—543).—$CH_2R{\cdot}CPh_2{\cdot}OH$ (*A*) (R = Me, Et, Pr$^\beta$, or Bu$^\alpha$) with PhOH and $AlCl_3$ in light petroleum at room temp. gives $CHR{:}CPh_2$ and $CH_2R{\cdot}CPh_2{\cdot}C_6H_4{\cdot}OH$-*p*. $CPh_2Pr^\beta{\cdot}OH$ gives $PhPr^\beta$, $CPh_2{:}CMe_2$, *p*-$OH{\cdot}C_6H_4{\cdot}CH_2Ph$ (**I**), and *αα-diphenyl-α-p-hydroxyphenylisobutane* (**II**), b.p. 198—199°/1 mm. $CHMeEt{\cdot}CPh_2{\cdot}OH$ (prep. from $CHMeEt{\cdot}COCl$, MgPhBr, and a trace of I in boiling Et_2O), b.p. 126—127°/1 mm., gives CHPhMeEt, $CPh_2{:}CMeEt$, (**I**), and *αα-diphenyl-α-p-hydroxyphenyl-β-methylbutane*, b.p. 195—196°/1 mm. $CPh_2Bu^\alpha{\cdot}OH$ gives mostly $CPh_2Me{\cdot}CMe{:}CH_2$ with some *ββ-diphenyl-γ-p-hydroxyphenyl-γ-methylbutane*, b.p. 195—200°/1 mm. (p-*chlorobenzoate*, m.p. 183—184°), and $CPh_2Me{\cdot}CMe_2Cl$. With $AlCl_3$ in light petroleum, (**II**) gives $CPh_2{:}CMe_2$ only. $CHR{:}CPh_2$ gives the same products as does (*A*). *αα-Diphenyl-α-p-hydroxyphenylpropane*, m.p. 113—113·5°, b.p. 198—199°/1 mm. (*benzoate*, m.p. 106—106·5°; p-*bromobenzenesulphonate*, *forms*, m.p. 121° and 129°), -*butane*, b.p. 196—197°/1 mm. (3 : 5-*dinitrobenzoate*, m.p. 133—134°), -n-*pentane* (**III**), b.p. 182—183°/1 mm. (p-*chlorobenzoate*, m.p. 158—159°), and -n-*hexane*, b.p. 183—184°/1 mm., are described. The structure of (**III**) is proved by the following synthesis. *p*-$OMe{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$ (prep. from *p*-$OMe{\cdot}C_6H_4{\cdot}COCl$ and MgPhBr; identified as chloride, m.p. 122—123°) and $CH_2(CO_2H)_2$ at 120—130°, later 170—180°, give a product, converted by boiling 20% KOH–EtOH into *p*-$OMe{\cdot}C_6H_4{\cdot}CPh_2{\cdot}CH_2{\cdot}CO_2H$, the chloride from which with MgEtBr in Et_2O gives *p*-$OMe{\cdot}C_6H_4{\cdot}CPh_2{\cdot}CH_2{\cdot}COEt$, whence (**III**) is obtained by reduction (Clemmensen) and demethylation. *p*-$OMe{\cdot}C_6H_4{\cdot}MgBr$ and $CPh_2Bu^\gamma Cl$ in Et_2O and later alone at 90—100° give *αα*-diphenyl-*α*-*p*-anisyl-, b.p. 180—210°/3 mm., and thence *αα-diphenyl-α-p-hydroxyphenyl-neopentane* [*ββ-dimethylpropane*], b.p. 205—206°/1 mm. (p-*chlorobenzoate*, m.p. 169—170°). R. S. C.

Esters and ethers of 2 : 4-dinitro-6-*cyclo*hexylphenol.—See B., 1941, II, 108.

Preparation of 2-chlororesorcinol. R. F. Milligan and F. J. Hope (*J. Amer. Chem. Soc.*, 1941, **63**, 544).—5 : 2 : 4 : 1-$NO_2{\cdot}C_6H_2(OH)_2{\cdot}CO_2H$ and SO_2Cl_2 in boiling AcOH give the 3-*Cl*-derivative, m.p. 252° (decomp.), reduced by $SnCl_2$–HCl–AcOH to 3-*chloro-5-amino-β-resorcylic acid*, m.p. 220—222° (decomp.). The derived cryst. diazonium chloride with $SnCl_2$–KOH gives the Cl-acid, which in boiling, aq. HCl yields 2-*chlororesorcinol*, m.p. 97—98°. R. S. C.

Esters of 4 : 4′-dihydroxy-γδ-diphenylhexane.—See B., 1941, III, 108.

Esters of 4 : 4′-dihydroxy-αβ-diethylstilbene.—See B., 1941, III, 78.

Dihydroxy-1 : 2 : 5 : 6-dibenzanthracene, m.p. 340—350° (decomp.) [quinone, m.p. 350° ; Ac_2 derivative, m.p. 291° (quinone, m.p. 294—296°) ; Me_2 ether, m.p. 244—245° (quinone, m.p. 264°)].—See A., 1941, III, 290.

Amino-alkylphenols. W. H. Hartung, L. J. Minnick, and H. F. Koehler (*J. Amer. Chem. Soc.*, 1941, **63**, 507).—4 : 1 : 3-$C_6H_2R(OH)_2$, NH_4Cl, and $NaHSO_3$ in conc., aq. NH_3 at 240—250° give 70—80% of 5-*amino*-2-n-*propyl*-, m.p. 109—110° (*N*-Ac derivative, an oil), -n-*butyl*-, m.p. 132·3—133° (*N*-Ac derivative, m.p. 142—143°), -n-*amyl*-, m.p. 122—123° (*N*-Ac derivative, m.p. 147—147·5°), -n-*hexyl*-, m.p. 127·3—127·6° (N-*Ac* derivative, m.p. 130·1—130·3°), -n-*heptyl*-, m.p. 130·5—130·9° (N-*Ac* derivative, m.p. 141·2—141·8°), and -n-*octylphenol*, m.p. 129·5—130·3° (N-*Ac* derivative, m.p. 130·1—130·5°), which have no or negligible germicidal activity. R. S. C.

Derivatives of 4 : 4′-diaminodiphenyl sulphone.—See B., 1941, III, 79.

Walden inversion in the replacement of hydroxyl by halogen. E. D. Hughes, C. K. Ingold, and I. C. Whitfield (*Nature*, 1941, **147**, 206—207).—Mainly a discussion. All the common substituting agents (PCl_5, $SOCl_2$, HCl, PBr_5, etc.) produce inversion unless a sufficiently powerful assembly, crit. for each reagent, of electron-releasing groups at the seat of substitution reverses the result. Such an assembly is present in $CHPhBu^\alpha{\cdot}OH$ and $CHPhBu^\beta{\cdot}OH$. L. S. T.

Production of highly-purified vitamin-*A*.—See B., 1941, III, 110.

I-α-Naphthyl*cyclo*pentanol. R. D. Kleene (*J. Amer. Chem. Soc.*, 1941, **63**, 631).—This *substance*, m.p. 74—76°, is obtained (70%) from 1-$C_{10}H_7{\cdot}MgBr$ and *cyclo*pentanone in Et_2O–C_6H_6. R. S. C.

Reactions of atoms and free radicals in solution. III. Introduction of a thiol group into *cyclo*hexane. M. S. Kharasch and K. Eberly (*J. Amer. Chem. Soc.*, 1941, **63**, 625; cf. A., 1941, II, 117).—Passage of Cl_2 into an illuminated mixture of CS_2 and *cyclo*hexane (with a trace of C_5H_5N) at <40° causes the reactions: $Cl_2 \rightarrow (h\nu)\ 2Cl$; $RH + Cl \rightarrow R + HCl$; $R + CS_2 \rightarrow SR{\cdot}CS{\cdot}$; $R + Cl_2 \rightarrow RCl + Cl$; $SR{\cdot}CS{\cdot} + Cl_2 \rightarrow SR{\cdot}CSCl + Cl$; $SR{\cdot}CSCl + Cl_2 \rightarrow SR{\cdot}CCl_2{\cdot}SCl$ (**I**). Impure cyclo*hexyl dithiotrichlorocarbonate* (**I**) is isolated (as well as *cyclo*hexyl chloride and $CCl_3{\cdot}SH$) as an undistillable oil, whence *cyclo*hexyl mercaptan, b.p. 157—162° (HgCl derivative), is obtained by hot KOH–EtOH. R. S. C.

Condensations by sodium. XIX. Reactions of compounds with dichloro-ethers and mercuric chloride. A. A. Morton, J. T. Massengale, and T. R. P. Gibb, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 324—327; cf. A., 1940, II, 62, 77).—$(Cl{\cdot}[CH_2]_2)_2O$ (**I**) and $NaCH_2Ph$ (from NaPh and PhMe in light petroleum at 83°) at 32—35° give 37% of $(Ph{\cdot}[CH_2]_3)_2O$ and 15% of Ph_2. After interaction of (**I**) with NaPh and *n*-$C_5H_{11}Na$, carbonation gives only a little $(CH_2{\cdot}CO_2H)_2$ and, from NaPh, $Ph{\cdot}[CH_2]_2{\cdot}OH$. $(CH_2Cl)_2O$ with NaR (R = CH_2Ph, Ph, or *n*-C_5H_{11}) gives a mixture of $(CH_2R)_2O$ and $CH_2R{\cdot}OH$. Na, activated by $C_5H_{11}{\cdot}OH$, has no effect on (**I**) in light petroleum at 35° or C_6H_6 at 70°. *n*-$C_5H_{11}Na$ and $HgCl_2$ in light petroleum at 25—35° give 46% of *Hg amyl chloride*, m.p. 121—122°, and some HgCl and Hg, but no $Hg(C_5H_{11})_2$. R. S. C.

Identification of organic compounds. IV. Triphenylmethyl ethers of cellosolves, carbitols, and related glycols. (Miss) M. K. Seikel and E. H. Huntress (*J. Amer. Chem. Soc.*, 1941, **63**, 593—595; cf. A., 1940, II, 233).—Ethers, (*a*) $OR{\cdot}[CH_2]_2{\cdot}O{\cdot}CPh_3$, where R = Me, m.p. 105·5—106° (lit. 104°), Et, m.p. 79—79·5° (lit. 77—78°), *Prβ*, m.p. 71—71·5°, *CH₂Ph*, m.p. 76—77°, *Ph*, m.p. 123·5—124°, p-*C₆H₄Buγ*, m.p. 121—121·5°, and H, m.p. 105—105·5° (lit. 102—103°), (*b*) $OR{\cdot}[CH_2]_2{\cdot}O{\cdot}[CH_2]_2{\cdot}O{\cdot}CPh_3$, where R = *H*, m.p. 112·5—113·5°, and *Me*, m.p. 58—59°, (*c*) ethylene, m.p. 187—188° (lit. 185—186°), *diethylene*, m.p. 157·5—158°, and *triethylene*, forms, m.p. 142—142·5° (stable) and 130·5—131°, $(CPh_3)_2$ *ether* are prepared by a simplified process. The ethers tend to undergo alcoholysis or hydrolysis when solutions in EtOH or aq. EtOH are boiled for a long time. R. S. C.

***X*-Ray crystallography and chemistry of the steroids.**—See A., 1941, I, 155.

Production of large crystals of ergosterol.—See B., 1941, III, 79.

Dehalogenation of 6-chloro-3-benzoyloxy-Δ⁴-cholestene. F. S. Spring and G. Swain (*J.C.S.*, 1941, 83—88; cf. A., 1939, II, 477).—α-Cholesteryl benzoate oxide (**I**) [the compound described by Lettré *et al.* (A., 1937, II, 455) is incorrectly described or is a mixture] and the β-isomeride (**II**) are unchanged by $SOCl_2$–C_5H_5N or $NPhMe_2$. (**I**) is stable to prolonged heating at 270°/13 mm., but (**II**) (0·5 hr.) yields (**I**) and a little of a *compound*, $(C_{27}H_{42}O)_3$, m.p. 300—302° (decomp.), $[\alpha]_D^{22}$ −16·5° (all rotations are in $CHCl_3$). 6-Chloro-3-benzoyloxy-Δ⁴-cholestene (**III**) is converted by Al–Hg in moist Et_2O into Δ³·⁵-cholestadiene, m.p. 80—81°, $[\alpha]_D^{20}$ −129·6°. (**III**) when refluxed with KOAc–EtOH yields isomeric *Et₁ ether benzoates*, viz., (**IV**), m.p. 166—167°, $[\alpha]_D^{20}$ −47·2°, and (**V**), m.p. 131—132°, $[\alpha]_D^{20}$ −29·4°, of either *cis*-3 : 4-dihydroxy-Δ⁵- (**VI**) or 3 : 6-dihydroxy-Δ⁴-cholestene, together with (probably) the 4-*monobenzoate* (**VII**), m.p. 153—154°, $[\alpha]_D^{20}$ −27·8°, of (**VI**) (cf. A., 1941, II, 63). (**VII**) and BzCl–C_5H_5N afford *cis*-3 : 4-dibenzoyloxy-Δ⁵-cholestene; Ac_2O–C_5H_5N give (probably) 4-*benzoyloxy*-3-*acetoxy*-Δ⁵-*cholestene*, m.p. 130—131°, $[\alpha]_D^{20}$ −54·8° [hydrolysed to (**VI**)], which differs from *cis*-3-benzoyloxy-4-acetoxy-Δ⁵-cholestene (Rosenheim *et al.*, A., 1937, II, 191) and is obtained also from 4-hydroxy-3-acetoxy-Δ⁵-cholestene and BzCl–C_5H_5N. Hydrolysis (MeOH–KOH) of (**IV**) and (**V**) affords the *diol Et₁ ethers*, m.p. 123—124°, $[\alpha]_D^{20}$ −59·2°, and 122—123°, respectively (neither gives a digitonide), which give *acetates*, m.p. 120—121°, $[\alpha]_D^{20}$ −83·5°, and m.p. 150°, respectively. A. T. P.

Tropic acid amide and its *N*-derivatives.—See B., 1941, III, 79.

Hydrogenation of aryl esters. W. R. McClellan and R. Connor (*J. Amer. Chem. Soc.*, 1941, **63**, 484—487).—In presence of Cu chromite, hydrogenation of RCO_2Ph (R = Et, Pr^n) at 250° gives 81—82% of $CH_2R{\cdot}OH$ and 86—98% of *cyclo*hexanol (**I**); $CHPh{:}CH{\cdot}CO_2Ph$ affords $Ph{\cdot}[CH_2]_3{\cdot}OH$ (81%) and (**I**) (82%); PhOBz gives 69% of PhMe and 87% of (**I**); Ph_2CO_3 gives 75% of MeOH and 82% of (**I**); *o*-$C_6H_4\langle^{O{\cdot}CH_2}_{O{\cdot}CO}$ (**II**) gives only (77%) *o*-$OH{\cdot}C_6H_4{\cdot}O{\cdot}[CH_2]_2{\cdot}OH$ (**III**). However, with H_2–Raney Ni at 200° or 250°, RCO_2Ph (R = Et, Pr^n) and $Pr^{\beta}CO_2C_6H_4Me$-*p* give 20—25% of the *cyclo*hexyl ester with 20—60% of RCO_2H + *cyclo*hexane (**IV**) [or methyl*cyclo*hexane (**V**)]; $CHPh{:}CH{\cdot}CO_2Ph$ affords *cyclohexyl* β-cyclo*hexylpropionate* (35—49%), b.p. 135—136°/4 mm., the free acid (17—25%), and (**IV**). Ph_2CO_3 gives (at 185—190°) only (**I**) and (**IV**); (**IV**) is obtained owing to cleavage of the ester and not from (**I**), which is unchanged by H_2–Raney Ni at 200°. PhOBz gives mainly (45%) (**I**) + (**V**) with 20—27% of *cyclo*hexyl hexahydrobenzoate, hexahydrobenzoic acid, and (**IV**); (**V**) is probably formed from the intermediate $CH_2Ph{\cdot}OH$. (**II**) gives 60% of β-2-*hydroxy*-cyclo*hexyloxyethyl alcohol*, b.p. 175—176°/36 mm., 25% of (**I**), and 20% of $(CH_2{\cdot}OH)_2$; the primary product is (**III**), since with H_2–Raney Ni this gives the same products. Small amounts (<10%) of RCO_2CH_2R are also formed in presence of Raney Ni, probably owing to slight hydrogenolysis to $CH_2R{\cdot}OH$ + (**I**) (cf. Cu chromite). Raney Ni stored under EtOH retains ~17% of EtOH and leads to Et esters in the above reactions, but the absorbed EtOH is removed by keeping under Et_2O or (**V**) for some hr. $CHPh{:}CH{\cdot}CO_2Et$ and H_2–Raney Ni at 180° give Et β-*cyclo*hexylpropionate (88%).
R. S. C.

Synthesis of 3′-fluoro-*dl*-thyronine and its iodinated derivatives. C. Niemann, J. F. Mead, and A. A. Benson (*J. Amer. Chem. Soc.*, 1941, **63**, 609—611).—4 : 2 : 1-$NO_2{\cdot}C_6H_3(NH_2){\cdot}OMe$ [prep. from 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}OMe$ by Na_2S–$NaHCO_3$], m.p. 117—118°, gives by way of the diazonium borofluoride 4% of 4 : 2 : 1-$NO_2{\cdot}C_6H_3F{\cdot}OMe$, m.p. 104—104·5° [obtained in 53% yield from *o*-$C_6H_4F{\cdot}OMe$ by AcOH–HNO_3 (*d* 1·5) in Ac_2O at −10°, later 25°], which is hydrogenated (PtO_2; 1 : 1 MeOH–EtOH) to 4 : 2 : 1-$NH_2{\cdot}C_6H_4F{\cdot}OMe$. A diazo-reaction ($Na_2SO_4$–$H_2SO_4$) then gives 4 : 3 : 1-$OMe{\cdot}C_6H_4F{\cdot}OH$, m.p. 54—55°, b.p. 90°/0·4 mm., which with 3 : 4 : 5 : 1-$C_6H_2I_3{\cdot}NO_2$ and K_2CO_3 in boiling $COMePr^{\alpha}$ gives 79% of 2 : 6-*di-iodo-3′-fluoro-4-nitro-4′-methoxydiphenyl ether*, m.p. 127—129°, reduced by $SnCl_2$–AcOH to the 4-NH_2-derivative [*hydrochloride* (**I**), m.p. 200° after sintering; *Ac* derivative, m.p. 199—200°]. With BuO·NO in AcOH, followed by aq. KCN–$CuSO_4$, (**I**) gives 3 : 5-*di-iodo-4-3′-fluoro-4′-methoxyphenoxybenzonitrile* (67%), m.p. 115—117°, b.p. 250° (bath)/0·1 mm., hydrolysed by 1 : 1 AcOH–HI (*d* 1·7) to 3 : 5-*di-iodo-4-3′-fluoro-4′-hydroxyphenoxybenzoic acid*, m.p. 237—238°, and reduced by $SnCl_2$–HCl–Et_2O at 0° to the substituted *benzaldehyde* (68%), m.p. 106—108° (p-*nitrophenylhydrazone*, m.p. 263—264°). Thence is obtained 5-*keto*-2-*phenyl*-4-3′ : 5′-*di-iodo-4′-3″-fluoro-4″-methoxyphenoxybenzylidene*-4 : 5-*dihydro-oxazole*, m.p. 180—190°, which with boiling 1% NaOH–70% EtOH gives α-*benzamido*-β-3 : 5-*di-iodo-4-3′-fluoro-4′-methoxyphenoxyphenylacrylic acid*, m.p. 238—240°, and with red P–HI–Ac_2O gives 3 : 5-*di-iodo-3′-fluoro*-dl-*thyronine*, m.p. 248° (decomp.), converted by H_2–Pd–$CaCO_3$ in N-KOH into 3′-*fluoro*-dl-*thyronine*, m.p. 238° (decomp.), and by KI_3 into 7N-aq. NH_3 into 3 : 5 : 5′-*triiodo-3′-fluoro*-dl-*thyronine*, m.p. 201° (decomp.). R. S. C.

Kinetics of hydrolysis of acid halides by water.—See A., 1941, I, 119.

Action of trimethylgallazide on naphthols. R. O. Pepe (*Anal. Asoc. Quím. Argentina*, 1940, **28**, 143—146; cf. A., 1940, II, 277).—3 : 4 : 5 : 1-$(OMe)_3C_6H_2{\cdot}CO{\cdot}N_3$ in $COMe_2$ with α- and β-$C_{10}H_7{\cdot}OH$ in 3N-NaOH yields α-, m.p. 155°, and β-$C_{10}H_7$ 3 : 4 : 5-*trimethoxybenzoate*, m.p. 127°, respectively.
F. R. G.

Synthesis of derivatives of *s*-diphenylethane related to materials occurring naturally. III. Relationship between benzylidenephthalide and benzyl*iso*quinoline alkaloids. S. Natelson and S. P. Gottfried (*J. Amer. Chem. Soc.*, 1941, **63**, 487—489; cf. A., 1939, II, 313).—*o*-$CO_2Et{\cdot}C_6H_4{\cdot}CH{:}CHPh$, b.p. 215°/15 mm., and 50% N_2H_4,H_2O in (best) EtOH at 110° give *stilbene-2-carboxylhydrazide*, m.p. 135°, the p-$C_6H_4Me{\cdot}SO_2$ derivative, m.p. 190°, of which with K_2CO_3 and glycerol at 205° gives stilbene-2-aldehyde, m.p. 83° (other methods of prep. are less good) (*phenylhydrazone*, m.p. 138°), which gives 5-*keto*-2-*phenyl*-4-o-*styrylbenzylidene*-4 : 5-*dihydro-oxazole*, m.p. 141°, and 5-o-*styrylbenzylidenerhodanine*, m.p. 195—196°. Benzylidenephthalide and conc., aq. NH_3 in EtOH at 90° give (cf. Gabriel *et al.*, A., 1879, 245; 1885, 902) o-*phenylacetylbenzamide*, m.p. 168°, and thence by boiling Ac_2O–AcOH 1-*keto*-3-*benzylidenedihydroisoindole*, m.p. 180°, which with H_2–PtO_2 in AcOH at 50 lb. gives the 3-CH_2Ph derivative, m.p. 157° (lit. 137°). R. S. C.

Alkyl and alkylamine esters of *p*-aminothiolbenzoic acid and related compounds.—See B., 1941, III, 78.

Synthesis of local anæsthetics of the diphenyl series. F. H. Case and E. Koft, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 508—510).—Coupling of 1 : 2 : 4-$C_6H_3MeI{\cdot}NO_2$ (**I**) gives poor yields of Ph_2 derivative. Better yields are obtained by oxidising (**I**) by $KMnO_4$ and coupling the resulting acid. The best method of obtaining 5 : 5′-dinitrodiphenic acid, m.p. 288°, is to treat 1 : 4 : 2-$CO_2H{\cdot}C_6H_3(NO_2){\cdot}N_2Cl$ with NH_2OH,HCl–KOH–$CuSO_4$–NH_3. The derived diacid chloride (prep. by PCl_5, not $SOCl_2$) with $NEt_2{\cdot}[CH_2]_2{\cdot}OH$ in PhMe, first cold and then boiling, gives *di-β-diethylaminoethyl* 5 : 5′-*dinitrodiphenate*, m.p. 67—68°, reduced catalytically in EtOH to *di-β-diethylaminoethyl* 5 : 5′-*diaminodiphenate* (**II**), m.p. 64—65°. β-*Diethylaminoethyl* 4-*nitro*-, m.p. 52—53° (*hydrochloride*, m.p. 186—188°), and 4-*amino-diphenyl-4′-carboxylate* (**III**), m.p. 78—79°, are similarly obtained from *p*-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO_2H$-*p*. (4 : 3 : 1-$NH_2{\cdot}C_6H_3Me{\cdot})_2$ and KNO_3 in oleum at <6°, later room temp., give the 6 : 6′-$(NO_2)_2$-derivative, m.p. 220—221°, which affords (diazo-reaction; EtOH) (2 : 5 : 1-$NO_2{\cdot}C_6H_3Me{\cdot})_2$, m.p. 158—159°. CrO_3–AcOH then yields 2 : 2′-*dinitrodiphenyl*-5 : 5′-*dicarboxylic acid*, m.p. 327—328° (decomp.) [Me_2 ester (**IV**), m.p. 167—168°], the *di-β-diethylaminoethyl* ester, +H_2O, m.p. 80—81°, and anhyd., an oil [*dihydrochloride*, m.p. 215—216° (decomp.); in MeOH gives (**IV**)], of which is reduced by Sn–HCl at <45° to the 2 : 2′-*diaminodiphenyl*-5 : 5′-*dicarboxylate* (**V**), m.p. 91—92°. (**II**), (**III**), and (**V**) are potent anæsthetics. R. S. C.

Synthesis with dienes : conjugation of a double bond with an aromatic nucleus. I. Condensation of anethole with maleic anhydride. W. Lora Tamayo and D. Ayestarán (*Anal. Fís. Quím.*, 1940, **36**, 44—50).—Anethole (but not esdragole) gives with maleic anhydride in PhMe at 180° (bath) the *anhydride*, m.p. 310—312°, of 7-*methoxy*-3-*methyl*-1 : 2 : 3 : 9-*tetrahydronaphthalene*-1 : 2-*dicarboxylic acid*, m.p. 292° (*Ag* salt, $C_{14}H_{15}O_5Ag,2C_{14}H_{16}O_5$). F. R. G.

3 : 3 : 5-Trimethyl*cyclo*hexenylformaldehyde. H. Barbier (*Helv. Chim. Acta*, 1940, **23**, 793—795).—3 : 3 : 5-Trimethyl*cyclo*hexylformaldehyde (**I**) and Br in $CHCl_3$ + $CaCO_3$ at ~0° give the 1-Br-derivative (**II**), b.p. 75°/3 mm., which with an excess of $NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2$ in aq. EtOH–AcOH affords the *semicarbazone*, m.p. 172°, of 3 : 3 : 5-trimethyl-$\Delta^{1\text{ or }6}$-*cyclo*hexenylformaldehyde, b.p. 59°/3 mm., 207° (corr.)/715 mm. (cf. Merling *et al.*, A., 1909, i, 479). The usual methods of elimination of HBr from (**II**) lead to undistillable resins. The Me_2 *acetal*, b.p. 69°/3 mm., of (**I**) could not be brominated; an acetal could not be prepared from (**II**). H. B.

Kinetics of thermal decomposition of acetophenone.—See A., 1941, I, 118.

***cis*- and *trans*-β-Aroyl-αβ-dimethylacrylic [β-aroyl-α-methylcrotonic] acids with particular reference to the open-chain and cyclic forms of the *cis*-derivatives.** R. E. Lutz and M. Couper (*J. Org. Chem.*, 1941, **6**, 77—90; cf. A., 1933, 502).—*Me* trans-β-p-*xenoyl*-α-*methylcrotonate* (**I**), m.p. 83·5—84°, obtained from Ph_2, $AlCl_3$, and the chloride (*A*) of Me H dimethylfumarate in CS_2, is hydrolysed mainly to the trans-*acid* (**II**), m.p. 152—153°, by KOH in 60% MeOH–H_2O whereas in anhyd. MeOH the main product is the cis-*acid* (**III**), m.p. 162°. Since pre-formed (**II**) is stable to alkali under the conditions used, the stereochemical rearrangements involve the ester itself or some intermediate. Esterification (CH_2N_2 or MeOH–H_2SO_4) of (**II**) produces (**I**) exclusively. Acid hydrolysis of (**I**) gives a small yield of (**III**); (**I**) appears stable towards NaOMe–MeOH at room temp. Gradual addition of Ph_2 in CS_2 to a mixture of $(ClCMe{\cdot}CO)_2O$ and $AlCl_3$ at room temp. followed by heating gives (**III**) accompanied by 2-*keto*-5 : 5-*di*-p-*xenyl*-3 : 4-*dimethyl*-2 : 5-*dihydrofuran*, m.p.

215—218° (decomp.), particularly when more than a min. proportion of Ph_2 is used. Probably (**III**) has the cyclic structure $\begin{matrix}CMe\cdot C(C_{12}H_9)(OH)\\ CMe\text{———}CO\end{matrix}>O$ since it is insol. in aq. $NaHCO_3$ and only very slowly sol. in aq. Na_2CO_3. It is oxidised by $KMnO_4$ to *p*-$C_6H_4Ph\cdot CO_2H$. (**III**) is converted by CH_2N_2 into the open-chain *Me* ester (**IV**), m.p. 101°, and by boiling H_2SO_4–MeOH into the cyclic Me ester [*2-keto-5-methoxy-5-p-xenyl-3 : 4-dimethyl-2 : 5-dihydrofuran*] (**V**), m.p. 121·5°. Alkaline hydrolysis of (**IV**) or (**I**) regenerates (**III**), also obtained by acid hydrolysis of (**V**). Isomerisation of (**IV**) to (**V**) is achieved by boiling MeOH–H_2SO_4 or by NaOMe–MeOH at room temp. (**III**) is converted by $SOCl_2$, PCl_5, or AcCl into the *ψ-chloride* (**VI**), $\begin{matrix}CMe\cdot C(C_{12}H_9)Cl\\ CMe\text{———}CO\end{matrix}>O$, m.p. 122—125·5° (decomp.), hydrolysed by moist air to (**III**) and transformed by MeOH or MeOH–AcOH–HCl into (**V**); under the latter conditions (**III**) and (**IV**) are unchanged. (**II**) or (**III**) is converted by HBr–AcOH into the *ψ-bromide*, m.p. 141·—144° (decomp.). Cu-bronze and (**VI**) in boiling C_6H_6 give 5 : 5′-*di*-(*2-keto-5-p-xenyl-3 : 4-dimethyl-2 : 5-dihydrofuran*), m.p. 231—234° (decomp.). PhBr, (*A*), and $AlCl_3$ in CS_2 give *Me* trans-*β*-p-*bromobenzoyl-α-methylcrotonate*, m.p. 70—70·5°, hydrolysed by AcOH in 60% MeOH to the trans-*acid*, m.p. 128·5—129·5°, slowly sol. in cold $NaHCO_3$ and converted into the same ester by CH_2N_2 and MeOH–H_2SO_4; the ester is inverted by prolonged contact with NaOMe–MeOH at room temp. Addition of PhBr in CS_2 to $(CMe\cdot CO)_2O$ and $AlBr_3$ in CS_2 leads to cis-*β*-p-*bromobenzoyl-α-methylcrotonic acid* (**VII**), m.p. 120—121°; under analogous conditions reaction is not observed with $AlCl_3$, but under more drastic conditions and with use of $PhNO_2$ only resinous products are obtained. At room temp. (**VII**) and CH_2N_2 give the open chain cis-*Me* ester, m.p. 87°, hydrolysed and rearranged by KOH–MeOH at room temp. to (**VII**) (71%) and the *ψ-Me* ester (10%) (**VIII**), m.p. 91·5°. (**VII**) and boiling H_2SO_4–MeOH give (**VIII**). *cis-β*-Benzoyl-*α*-methylcrotonic acid (**IX**) is insol. in cold but sol. in warm aq. $NaHCO_3$, in which the *trans*-acid dissolves immediately with effervescence. *Me* cis-*β-benzoyl-α-methylcrotonate*, m.p. 60°, obtained from (**IX**) and CH_2N_2–Et_2O, is hydrolysed (KOH–MeOH at room temp.) to (**IX**) and rearranged to the cyclic form by MeOH–H_2SO_4. Attempts to prepare *cis-β*-trimethylbenzoyl-*α*-methylcrotonic acid were unsuccessful. H. W.

Reduction of *cis-* and *trans-β-p-*xenoyl-*αβ*-dimethylacrylic [*β-p-*xenoyl-*α*-methylcrotonic] acids and their esters. R. E. Lutz and M. Couper (*J. Org. Chem.*, 1941, **6**, 91—104).—Reduction ($SnCl_2$, $Na_2S_2O_4$, or Zn + AcOH) of *cis-β-p-*xenoyl-*α*-methylcrotonic acid (**I**) gives *γ-xenyl-αβ-dimethyl-*Δ^{α}*-buteno-γ-lactone* (**II**), m.p. 133·5°, which is stable towards H_2SO_4–Ac_2O, Br in $CHCl_3$, $SnCl_2$–HCl–AcOH, and boiling H_2SO_4–MeOH; it is converted by NH_3–$AgNO_3$–NaOH into 5 : 5′-di-(2-keto-5-*p*-xenyl-3 : 4-dimethyl-2 : 5-dihydrofuran) (**III**). (**II**) is transformed by KOH–MeOH at room temp. into a mixture of *β-p-xenoyl-α-methylbutyric acid* A (**IV**), m.p. 198·5—200·5°, and B (**V**), m.p. 164—165°. (**IV**) is stable towards the various reducing combinations but is converted by boiling AcCl into (**II**). The *Me* ester (**VI**), m.p. 116°, prepared from (**IV**) by CH_2N_2 or boiling MeOH–H_2SO_4, is hydrolysed by alkali to a mixture of (**IV**) and (**V**). (**V**) is stable towards aq. Na_2CO_3 and $Na_2S_2O_4$; its *Me* ester (**VII**), m.p. 73°, obtained by use of CH_2N_2 or MeOH–H_2SO_4, is converted by short treatment with KOH–MeOH at room temp. into (**VI**) and then hydrolysed to (**IV**). (**IV**) or (**V**) is transformed by short treatment with H_2SO_4–Ac_2O at room temp. into *2-keto-5-p-xenyl-3 : 4-dimethyl-2 : 3-dihydrofuran*, m.p. 93·5—95°, which is immediately converted by Tollens' reagent into (**III**), gives a non-cryst. compound with Br in CCl_4, and is isomerised to (**II**) by boiling Ac_2O, by NH_3 in hot EtOH, or by $Na_2S_2O_4$ in boiling 70% EtOH. Alkaline hydrolysis converts it into (**IV**) whilst $SnCl_2$–$SnCl_4$–HCl–AcOH transforms it into (**II**) and (**IV**). $Na_2S_2O_4$ is without action on (**I**) in boiling 70% MeOH but after addition of Na_2CO_3 (**II**) is obtained in very good yield. Zn dust and AcOH give poor yields of (**II**) from (**I**). With Zn dust and saturated aq. Na_2CO_3 at 80—90° (**I**) gives (**IV**) with some (**V**) but no (**II**), which is stable under these conditions. Reduction (Zn dust and conc. AcOH) of the open-chain Me ester of (**I**) leads to (**VI**) and (**VII**). *trans-β-p-*Xenoyl-*α*-methylcrotonic acid was reduced (Zn dust and conc. AcOH at room temp.) mainly to (**V**) whereas only ill-defined products are obtained when $Na_2S_2O_4$ is used, and a mixture of (**IV**) and (**V**) when Zn dust and aq. Na_2CO_3 are employed. The *trans*-Me ester, Zn dust, and boiling AcOH afford a mixture of (**VI**) and (**VII**) whilst (**II**) results under the action of $SnCl_2$–conc. AcOH and HCl. Catalytic reduction (PtO_2) of (**II**) in abs. EtOH proceeds slowly but continuously and after absorption of 1·5—2 mols. of H_2 gives mainly *γ-p-xenyl-αβ-dimethylbutyrolactone* (**VIII**), m.p. 151°, also obtained in small yield by reduction of (**IV**) with a large excess of Na and EtOH. Some (**VIII**) results from the catalytic reduction of the labile enol lactone $\begin{matrix}CMe{:}C(C_{12}H_9)\\ CHMe\text{——}CO\end{matrix}>O$ but the main product is (**II**) formed by rearrangement. Hydrolysis (10% NaOH) in one case only of (**VIII**) gives an *acid*, m.p. 110—113·5° (decomp.), passing above its m.p. into (**VIII**). *γ-Phenyl-αβ-dimethyl-*Δ^{α}*-buteno-lactone*, b.p. 141°/21 mm., is obtained by the action of Na_2CO_3–$Na_2S_2O_4$ or $SnCl_2$–conc. HCl–AcOH on *cis-β*-benzoyl-*α*-methylcrotonic acid. It immediately reduces Tollens' reagent. It is hydrolysed by KOH–MeOH at room temp. to *β*-benzoyl-*α*-methylbutyric acid (**IX**), new m.p. 150—152°. The *Me* ester, b.p. 137—139°/2—3 mm., obtained by means of CH_2N_2 or MeOH–HSO_4 is hydrolysed (KOH–EtOH at room temp.) to (**IX**) and does not give a cryst. semicarbazone. H. W.

Synthesis of veratroylacetaldehyde and influence of hydroxyl groups on the reactivity of the *p*-carbonyl group. L. Brickman, W. L. Hawkins, and H. Hibbert (*Canad. J. Res.*, 1941, **19, B**, 24—33).—Vanilloylacetaldehyde could not be synthesised starting with vanillin (**I**). With $CH_2{:}CH\cdot CH_2\cdot MgBr$ (**II**), (**I**) gives an oil (OMe 17·7%), b.p. 160—220° (bath temp.)/0·01 mm., whilst its benzoate does not react; *O*-methoxymethylvanillin yields the corresponding *carbinol* (poor yield), m.p. 70—71°, which with CrO_3 affords a resin. 3 : 4 : 1-$(OMe)_2C_6H_3\cdot CHO$ and (**II**) yield *α*-3 : 4-*dimethoxyphenyl-*Δ^{γ}*-buten-α-ol*, m.p. 80·5—81·5°, oxidised (CrO_3) to *ω-vinylacetoveratrone*, m.p. 58° (*semicarbazone*, m.p. 140—142°), which with O_3 in AcOH or EtOAc followed by Zn dust–H_2O–Et_2O gives an amorphous product. Acetovanillone acetate (**III**) with Br in $CHCl_3$ yields the *ω-Br*-derivative; m.p. 86—87·5°, which with KCN in EtOH gives the *ω-CN*-compound, m.p. 191—192°; and with MeOH–conc. HCl yields *ω-chloro-*, m.p. 102—103°, and thence *ω-cyano-acetovanillone*, m.p. 152—153°. Neither nitrile is reduced by $SnCl_2$ + HCl in Et_2O. With HCO_2Et and Na in C_6H_6, (**III**) yields acetovanillone; *O-methoxymethylacetovanillone*, m.p. 52—53°, gives (?) *α*-3-*methoxy-4-methoxymethoxyphenylacrylic acid*, m.p. 58—59°, and acetoveratrone affords (cf. A., 1940, II, 348) veratroylacetaldehyde (90%), b.p. 180—230° (bath temp.)/0·1 mm. (with polymerisation) (*Cu* derivative; *semicarbazone*, m.p. 181—182°). The influence of *p*-OH on the reactivity of CO-compounds is discussed. A. Li.

Action of ammonia and hydrazoic acid derivatives on semicarbazones, oximes, and semioxamazones of Δ^2-*cyclo*hexenones. I. Matzurevitsch (*Bull. Sci. Univ. Kiev*, 1939, No. 4, 7—22).—NH_2OH and the semicarbazones (*A*) of 3-methyl- (**I**) or 3 : 5-dimethyl-Δ^2-*cyclo*hexenone (**II**) in EtOH yield the corresponding hydroxylamino*cyclo*hexanone oximes; NH_2OH does not react with the C:C of (*A*). Conversely, the action of semicarbazide on the oximes of (**I**), (**II**), 5-phenyl-3-methyl- (**III**), or 5-furyl-3-methyl-Δ^2-*cyclo*hexenone (**IV**) gives the corresponding semicarbazido-semicarbazones. The *semioxamazones* of (**I**), m.p. 196—197° (decomp.), (**II**), m.p. 197—198° (decomp.), (**III**), m.p. 179—180° (decomp.), and (**IV**), m.p. 175—176° (decomp.), with semicarbazide yield the corresponding semicarbazones. R. T.

Constitutions of eremophilone, hydroxyeremophilone, and hydroxydihydroeremophilone. IV. A. E. Gillam, J. I. Lynas-Gray, A. R. Penfold, and J. L. Simonsen (*J.C.S.*, 1941, 60—68).—Whilst additional evidence is advanced in support of the structure previously assigned (A., 1939, II, 117) to eremophilone (**I**), it is now suggested that hydroxyeremophilone (**II**) and hydroxydihydroeremophilone (**III**) are 1-hydroxy-2-keto-5 : 10-dimethyl-3-*iso*propylidene-$\Delta^{1:9}$-octahydronaphthalene and 2-hydroxy-1-keto-5 : 10-dimethyl-3-*iso*propyldecahydronaphthalene, respectively. Br and (**I**) in $CHCl_3$ give *tetrabromoeremophilone*, decomp. 116°, whilst (**I**) is reduced [$Al(OPr^{\beta})_3$–$Pr^{\beta}OH$] to *eremophilol*, b.p. 164—165°/13 mm., $[\alpha]_{5461}$ −55·6° in MeOH (3 : 5-*dinitrobenzoate*, m.p. 88—89°, $[\alpha]_{5461}$ −149·4° in EtOAc). Ozonolysis of (**I**) affords CH_2O and a CO-acid (impure *Me* ester, b.p. ~220°/18 mm.), oxidised (NaOBr) to a *γδ*-dimethylheptane-*αδζη*-

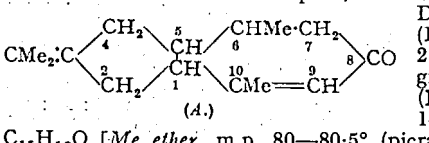
tetracarboxylic acid (Ag_3 salt; Me_4 ester, b.p. 203—205°/5 mm., $[\alpha]_{5461}$ −17·5° in MeOH), the structure of which confirms that of (**I**). The Me ether of (**II**) and H_2 (Pd–C, EtOH) give the impure H_4-ether (2 : 4-*dinitrophenylhydrazone*, m.p. 140°), which with MgMeI affords a product dehydrogenated (Se) to 1 : 6 : 7-$C_{10}H_5Me_2Pr^{\beta}$. The absorption spectra of (**II**) and related ketones have been studied and the results are discussed. The structures of various degradation products (cf. *loc. cit.*) are re-formulated.

F. R. S.

Chalkones : production of 1-keto-2-aryl-1 : 2 : 3 : 4-tetrahydronaphthalenes from chalkone dibromides through the related β-aroyl-α-arylpropionitriles. M. S. Hidayetulla, R. C. Shah, and T. S. Wheeler (*J.C.S.*, 1941, 111—112; cf. A., 1938, II, 18).—The following are prepared as previously described (*loc. cit.*) : β-$C_{10}H_7$ αβ-*dibromo*-β-p-*anisylethyl ketone*, m.p. 156°; β-2-*naphthoyl*-α-*phenyl*-, m.p. 128°, and -p-*anisyl*-*propionitrile*, m.p. 121°; β-p-*toluoyl*-α-p-*anisyl*-, m.p. 151°, β-2-*naphthoyl*-α-*phenyl*-, m.p. 187°, and β-2-*naphthoyl*-α-p-*anisyl*-*propionic acid*, m.p. 173°. The appropriate COAr·CH_2·CHAr'·CO_2H and Zn–Hg–HCl–PhMe afford γ-*phenyl*-α-p-*anisyl*-, m.p. 98°, α-*phenyl*-, m.p. 80°, and α-p-*anisyl*-γ-p-*tolyl*-, m.p. 115°, γ-*phenyl*- (**I**), m.p. 98°, and γ-p-*tolyl*-α-3 : 4-*methylenedioxyphenyl*- (**II**), m.p. 96°, and α-p-*anisyl*-γ-β-*naphthyl*-*butyric acid*, m.p. 132°. Cyclisation (boiling $POCl_3$) then affords 1-*keto*-2-p-*anisyl*-, m.p. 107° (*oxime*, m.p. 126°), -2-*phenyl*-7-*methyl*-, m.p. 67°, and -2-p-*anisyl*-7-*methyl*-, m.p. 108°, -1 : 2 : 3 : 4-*tetrahydronaphthalene*. (**I**) and (**II**) could not be cyclised.

A. T. P.

Volatile plant substances. XI. Constitution of β-vetivone. A. S. Pfau and P. A. Plattner (*Helv. Chim. Acta*, 1940, **23**, 768—792).—Reasons are advanced for assigning structure (*A*) to β-vetivone (**I**) (A., 1939, II, 331); dihydro-β-vetivone, which has not been obtained pure, is the 9 : 10-H_2-derivative.



(*A.*)

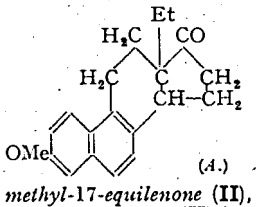
Dehydrogenation (Pd–C) of (**I**) at 270—285° in CO_2 gives vetivazulene (**II**) (A., 1939, II, 148), a naphthol, $C_{15}H_{16}O$ [*Me ether*, m.p. 80—80·5° (picrate, m.p. ~130°)], and a *phenol*, $C_{14}H_{16}O$ (**III**), probably 4-*methyl*-6-iso*propyl*-β-*naphthol*, m.p. 84—84·5° [*phenylcarbamate*, m.p. 134·5—135°; *Me ether*, m.p. 63·5—64° (*picrate*, m.p. 125·5—126°), reduced (H_2, PtO_2, AcOH) to a hydrocarbon which is dehydrogenated (Pd–C at 310—335° in CO_2) to eudalene (**IV**)]. The mixed *iso*vetivones previously described (*loc. cit.*) are dehydrogenated (Se at 265—300°/100—120 mm. in CO_2) to (**II**) and (**III**), whilst the hydrocarbon $C_{15}H_{24}$ (*loc. cit.*) with S or Se affords (**II**), vetivalene (1 : 5 : 7-$C_{10}H_5Me_2Pr^{\beta}$) (**V**), and a little (**IV**). The hydrocarbon $C_{15}H_{24}$ [prep. by Wolff–Kishner reduction of the semicarbazone of (**I**)] with S or Se gives, however, (**II**) and (**IV**). $PhPr^{\beta}$ and 2 : 6-$C_{10}H_6Me_2$ are produced from (**V**) and $AlBr_3$ in C_6H_6. Quant. ozonolysis of (**I**) yields 0·9 mol. of $COMe_2$. Dihydro-β-vetivol (**VI**), m.p. 107°, which is inactive, is oxidised (O_3 in aq. AcOH followed by Zn dust) to a *hydroxy-ketone*, $C_{12}H_{20}O_2$, m.p. 93—93·5°, dehydrated [$NaHSO_4$ at 200° (bath)/3 mm.] to a *ketone*, $C_{12}H_{18}O$ (**VII**) (semicarbazone, m.p. 198—199°) [an active ketone (**VII***a*), α_D −132° (*l* = 1) (*semicarbazone*, m.p. 198—199°, $[\alpha]_D$ −103° in AcOH), is similarly obtained from an active (**VI**) (mixture of isomerides)]. Reduction (Na, EtOH) of (**VII***a*), dehydration of the resulting alcohol, b.p. 115—120°/4 mm., and subsequent dehydrogenation (Se at 240—300°) gives 4 : 8-dimethylazulene (*picrate*, m.p. 150°). Reduction (H_2, Ni, EtOH) of (**VII**) yields the ketone, $C_{12}H_{20}O$, the *CHPh*: derivative, m.p. 72—73°, of which is oxidised (O_3 in $CHCl_3$ followed by aq. NaOH–H_2O_2) to 3 : 7-*dimethyl*cyclo*heptane*-1-*carboxylic*-2-*acetic acid*, m.p. 183—184° (decomp.). Wolff–Kishner reduction of (**VII**) gives a hydrocarbon, $C_{12}H_{20}$, b.p. 69—71°/2·5 mm., oxidised (O_3 in $CHCl_3$ followed by aq. $KMnO_4$) to dl-cyclo*pentane*-1-α-*propionic*-2-β-*butyric acid*, m.p. 168—169°. MeOH–30% H_2O_2–15% NaOH converts (**I**) into the 9 : 10-*oxide*, b.p. 146—149°/3·5 mm., which with boiling AcOH–NaOAc gives 9-*hydroxy*-β-*vetivone*, b.p. 165°/2 mm., m.p. 82—83°, $[\alpha]_D$ −74·5° in EtOH, and with AcOH–HCl affords a *compound*, $C_{15}H_{22}OCl_2$, m.p. 145°. Tetrahydro-β-vetivone and Br–AcOH yield the 7 : 9-Br_2-derivative, m.p. 206°, converted by boiling AcOH–Ac_2O–NaOAc into the 8 : 9-*diketone* (*hydroxydihydro*-β-*vetivone*), m.p. 81·5—82·5°, which gives a violet colour with EtOH–$FeCl_3$. Oxidation (CrO_3, AcOH, 90°) of tetrahydro-β-vetivol yields 4-iso*propyl*-cyclo*pentane*-1-α-*propionic*-2-β-*butyric acid*, m.p. 162·5—163·5°, which when distilled in a vac. with Ac_2O and some cryst. $Ba(OH)_2$ affords 5-keto-4 : 7-dimethyl-2-*iso*propylhydrindane (*semicarbazone*, m.p. 194—195°). This is dehydrogenated (Pd–C at 350°) to 5-*hydroxy*-4 : 7-*dimethyl*-2-iso*propylhydrindene*, m.p. 129°, also obtained in poor yield by KOH-fusion of the Na salt of 4 : 7-dimethyl-2-*iso*propylhydrindene-5-sulphonic acid (*Ag* salt) (prep. from the hydrocarbon and cold conc. H_2SO_4). The compounds prepared by catalytic reduction of (**I**) are all inactive owing presumably to a true internal compensation.

H. B.

Synthesis of analogues of sex hormones. An analogue of equilenin lacking the phenolic A ring. W. E. Bachmann and D. G. Thomas (*J. Amer. Chem. Soc.*, 1941, **63**, 598—602).—*Me* 1-*keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*glyoxylate* (prep. from 1-ketotetrahydronaphthalene by $Me_2C_2O_4$–NaOMe–C_6H_6–N_2 at room temp.), m.p. 65·5—66·5°, with powdered glass at 150° and later 180° gives *Me* 1-*keto*-1 : 2 : 3 : 4-*tetrahydro*-2-*naphthoate*, m.p. 84·5—86·5°, which with NaOMe and MeI in C_6H_6 gives the 2-*Me* derivative, m.p. 56·5—57·5°. The Reformatsky reaction then gives *Me* 1-*hydroxy*-2-*carbomethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetate*, m.p. 63·5—64·5°, dehydrated by $SOCl_2$–C_5H_5N–C_6H_6, followed by KOH–MeOH, to anti-2-*carboxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylideneacetic acid*, m.p. 194—195° (gas), and the *anhydride*, m.p. 139·5—141°, of the *syn*-isomeride. 2% Na–Hg in H_2O converts the derived K salts into α-, m.p. 167·5—169° (*Me*$_2$ ester, m.p. 62·5—64°), and β-2-carboxy-2-methyl-1 : 2 : 3 : 4-tetrahydro-1-naphthylacetic acid, m.p. (+solvent) ~110—115° (gas) (*anhydride*, m.p. 141·5—143°; Me_2 ester, an oil). The author's methods (cf. A., 1940, II, 225) then yield α-, m.p. 114·5—115°, and β-2-*carbomethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylacetic acid*, m.p. 107·5—109°, impure Me α- and β-2-carbomcthoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro-1-naphthylpropionate, *Me* α-, an oil, and β-3'-*keto*-2-*methyl*-1 : 2-cyclo*pentano*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2'-*carboxylate*, *forms*, m.p. 97—99·5° and 86—88°, α-, m.p. < room temp. [*semicarbazone*, m.p. 241—242° (decomp.; pre-heated bath)], and β-3'-*keto*-2-*methyl*-1 : 2-cyclo*pentano*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 57—58°, α-2-*carbomethoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthylpropionic acid*, m.p. 78—80·5°, Me α-2-carbomethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro-1-naphthylbutyrate, "sublimes" at 190—200°/0·5 mm., α-1-keto-11-methyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene, "sublimes" at 100—150°/0·6 mm. [2-CO_2Me-derivative, solidifies at ~—10°; *semicarbazone*, m.p. 210·5—212·5° (decomp.; preheated bath)], and α-11-methyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene, an oil [with Se at 310—320° gives phenanthrene].

R. S. C.

Synthesis of compounds related to sex hormones. A homologue of equilenin containing an *ang.* ethyl group. W. E. Bachmann and D. W. Holmes (*J. Amer. Chem. Soc.*, 1941, **63**, 595—598).—Addition of NaOMe–MeOH and then EtI to Me 1-keto-7-methoxy-1 : 2 : 3 : 4-tetrahydrophenanthrene-2-carboxylate in boiling C_6H_6 gives *Me* 1-*keto*-7-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-2-*carboxylate*, m.p. 103—104°, which with Zn–CH_2Br·CO_2Me gives *Me* 1-*hydroxy*-2-*carbomethoxy*-7-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylacetate*, m.p. 148·5—149·5°. $SOCl_2$–C_5H_5N, followed by KOH–MeOH and then Na–Hg–H_2O, gives α- (44%), m.p. 234—236° (decomp.), and β-2-*carboxy*-7-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylacetic acid* (45%), m.p. 210—213°. The derived (CH_2N_2–Et_2O) α-, m.p. 109·5—110·5°, and β-*Me*$_2$, m.p. 113—114°, esters with boiling NaOH–H_2O–MeOH give the α-, m.p. 141—142°, and β-2-*Me H* ester, m.p. 186—187°, and thence (Arndt–Eistert) *Me* α-, m.p. 86—87°, and β-2-*carbomethoxy*-7-*methoxy*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*phenanthrylpropionate*, m.p. 83·5—84·5°, cyclised by NaOMe–C_6H_6–N_2 to *Me* α-, m.p. 137—138° (vac.), and β-3-*methoxy*-19-*methyl*-17-*equilenone*-16-*carboxylate*, m.p. 167—168·5°. Boiling HCl–AcOH–N_2 then affords α-, m.p. 124·5—125·5°, and β-dl-3-*methoxy*- (*A*), m.p. 171—173° (vac.), and later α- (**I**), m.p. 219—220° (vac.), and β-dl-3-*hydroxy*-19-*methyl*-17-*equilenone* (**II**), m.p. 253—255° (vac.). The œstrogenic activity of (**II**) is of the same order as that of *dl*-equilenin; (**I**) is inactive.



(*A.*)

R. S. C.

Rates of reaction of stereoisomeric oximes of cholestenone and of benzylidene-*p*-bromoacetophenone with iodine monobromide.—See A., 1941, I, 119.

Hydration of acetylene derivatives of the *cyclo*pentanopolyhydrophenanthrene seires.—See B., 1941, III, 109.

Action of oxygen on colloidal solutions of cholesterol. O. Wintersteiner and S. Bergström (*J. Biol. Chem.*, 1941, **137**, 785—786).—Colloidal solutions of cholesterol with O_2 at 85° in presence of Na stearate yield 7(α)-hydroxy- (dibenzoate, m.p. 174°) and (mainly) 7-keto-cholesterol, and (?) 7-keto-cholesterylene. A. LI.

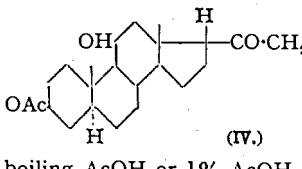
Nature of the androgens in female adrenal tumour urine. J. K. Wolfe, L. F. Fieser, and H. B. Friedgood (*J. Amer. Chem. Soc.*, 1941, **63**, 582—593; see also A., 1941, III, 369). —The steroids from the acid- (HCl) hydrolysed urine are freed from phenols by 2N-NaOH and from a considerable amount of colouring matter by aq. NaOH–$Na_2S_2O_4$. The neutral 17-keto-steroid or androgen fraction, isolated by Girard's reagent *T*, yields androsterone, $\Delta^{3:5}$-androstadien-17-one, 3(α)-hydroxyætiocholan-17-one, dehydro*iso*androsterone [isolated partly as *H succinate*, m.p. 257—259° (*Me* ester, m.p. 155·5—156·5°), partly as digitonide, and partly as 3-chloro-Δ^5-androsten-17-one which is formed during the hydrolysis], and a 3(α)-*hydroxyandrosten*-17-*one* (**I**), m.p. 181—183°, $[\alpha]_D^{26\cdot5}$ +122±2° in 95% EtOH [*acetate*, m.p. 178—180°, $[\alpha]_D^{23\cdot6}$ +114±5° in 95% EtOH; benzoate, m.p. 162—164°; semicarbazone, m.p. 279—280° (decomp.)]. (**I**) gives a faint yellow colour with $C(NO_2)_4$, is unaffected by boiling aq. EtOH–HCl, and is reduced [H_2, PtO_2, AcOH and subsequent acetylation (Ac_2O–C_5H_5N at 100°)] to androstane-3 : 17-diol diacetate. When the androstenedione (as Girard derivative) obtained by Oppenauer oxidation of (**I**) is polarographed, the curve shows the absence of C:C·CO; the double linking in (**I**) may, therefore, be at the 6 : 7, 7 : 8, 9 : 11, or 11 : 12 position. It is possible that (**I**) may be formed during the initial hydrolysis from ? androsta-3 : 11-diol-17-one. M.p. are corr. H. B.

Betaine hydrazone chloride (+H_2O), m.p. 233—234° (corr.; decomp.), of cholestanone. Dehydro*iso*androsterone-*p*-nitrophenylhydrazone acetate, m.p. 291—292° (corr.; decomp.).—See A., 1941, III, 269.

Keto-pregnane- and -pregnene-21-aldehydes.—See B., 1941, III, 79.

Preparation of sterol degradation products, *e.g.*, progesterone. —See B., 1941, III, 79.

Constituents of the adrenal cortex and related substances. XXXVIII. Conversion of substance *A* into substance *N*. C. W. Shoppee and T. Reichstein. **XXXIX. Chemical proof for the presence of oxygen in the 3-position.** C. W. Shoppee (*Helv. Chim. Acta*, 1940, **23**, 729—739, 740—746).—XXXVIII. The *triacetate* (**I**), m.p. 219—220°, $[\alpha]_D^{18}$ +74±2° in $COMe_2$ (prep. by Ac_2O–C_5H_5N at 20°), of substance *A* (**II**) is oxidised (CrO_3, AcOH, 20°) to allo*pregnane*-3(β) : 17 : 20 : 21-*tetraol*-11-*one* 3 : 20 : 21-*triacetate* (**III**), m.p. 208—210° or 183—184° resolidifying with m.p. 211—212°, $[\alpha]_D^{14}$ +69±3·5° in $COMe_2$, which is hydrolysed (MeOH–2N-NaOH) to allo*pregnane*-3(β) : 17 : 20 : 21-*tetraol*-11-*one* [the 11-dehydro-derivative of (**II**)], m.p. 160—170°, resolidifying with m.p. 212—216°. Zn dust and (**I**) in boiling PhMe yield the *compound* (**IV**) (designated 17-iso-R *diacetate*), m.p. 133°, resolidifying with m.p. 147—148°, $[\alpha]_D^{18}$ −60±1·5° in $COMe_2$, which reduces aq. NH_3–Ag_2O–MeOH at room temp. and is unaffected by short treatment with boiling AcOH or 1% AcOH–HCl. Oxidation (CrO_3, AcOH, room temp.) of (**IV**) affords the 11-*CO*-derivative (**V**) (designated 17-iso-N *diacetate*), m.p. 131—132° $[\alpha]_D^{14}$ −44±3° in $COMe_2$ [also obtained from (**III**) and Zn dust in boiling PhMe], which is converted by boiling EtOH–conc. HCl followed by Ac_2O–C_5H_5N at room temp. into the diacetate, m.p. 149°, $[\alpha]_D^{18}$ +77·5±2·5°, $[\alpha]_{5461}^{18}$ +99·5±2·5° in $COMe_2$, of substance *N*. (**V**) is unaffected by C_5H_5N at 115°/8 hr. or $MeNO_2$ at 100°/24 hr. but is decomposed by boiling $MeNO_2$–piperidine. M.p. are corr.



(IV.)

XXXIX. 17-iso*allo*-*Pregnane*-3(β) : 11 : 21-*triol*-20-*one* 3 : 21-*diacetate* [= (**IV**) (above)] is dehydrated by boiling for 15 min. with AcOH (90 vol.-%) + conc. HCl (10 vol.-%); acetylation (Ac_2O, C_5H_5N, room temp.) of the product gives a *compound*, $C_{25}H_{36}O_5$, m.p. 146—147° (softens at 142°), $[\alpha]_D^{17}$ +33±6° in $COMe_2$, which reduces aq. NH_3–Ag_2O at room temp. and, unlike (**IV**), gives a yellow colour with $CHCl_3$–$C(NO_2)_4$. Androstane-3(β) : 11-diol-17-one [from (**II**) and HIO_4] is similarly dehydrated to $\Delta^{11:12}$-androsten-3(β)-ol-17-one [the *acetate* (**VI**), m.p. 102°, $[\alpha]_D^{14}$ +110·8±4° in $COMe_2$, also obtained from androstane-3(β) : 11-diol-17-one 3-acetate and $KHSO_4$ at 135—140° (bath)/0·05 mm., gives a yellow colour with $C(NO_2)_4$]. Reduction (H_2, PtO_2, AcOH) of (**VI**) and subsequent acetylation (Ac_2O, C_5H_5N, 100°) yields androstane-3(β) : 17(*trans*)-diol diacetate, m.p. 129°, $[\alpha]_D^{14}$ −1±1° in $COMe_2$; the free diol (**VII**) is oxidised (CrO_3, AcOH, 20°) to androstane-3 : 17-dione, m.p. 132—134°, $[\alpha]_D^{14}$ +100·4±3° in EtOH. Since the positions and configurations of the OH in (**VII**) are established, proof is now afforded of the 3(β)-OH in (**II**) and compounds related to it. M.p. are corr. H. B.

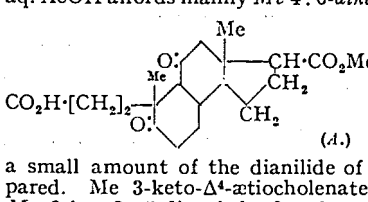
12-Hydroxy- and 12-keto-pregnane derivatives. T. Reichstein and E. von Arx (*Helv. Chim. Acta*, 1940, **23**, 747—753). —The Wieland degradation of deoxycholic acid is re-examined (cf. Hoehn *et al.*, A., 1938, II, 329; Sawlewicz, A., 1939, II, 265), the following intermediate compounds being described: αα-diphenyl-β-diacetoxybisnorcholanylethylene, m.p. 120—124° (Hoehn, 158—160°); diphenyl-3 : 12-dihydroxyternorcholanylcarbinol, m.p. 225—229° (corr.) (from MgPhBr and Me bisnordeoxycholate in Et_2O–C_6H_6), and its amorphous diacetate [dehydrated by boiling AcOH to αα-diphenyl-β-3 : 12-diacetoxyternorcholanylethylene, m.p. 216—217° (corr.)]. Pregnane-3(α) : 12-diol-20-one diacetate, m.p. 118—120°, is hydrolysed by aq. MeOH–K_2CO_3 at 20° to the 12-*monoacetate*, m.p. 208—210° (corr.), $[\alpha]_D^{17}$ +151·2±6°, $[\alpha]_{5461}^{17}$ +192·6±3° in $COMe_2$, which is hydrolysed (MeOH–KOH) to pregnane-3(α) : 12-diol-20-one (**I**) and oxidised (CrO_3, AcOH, 20°) to 12-*acetoxypregnane*-3 : 20-*dione*, m.p. 121—122°, $[\alpha]_D^{16}$ +141±3° in $COMe_2$ (also appears to exist in a modification, m.p. ~180°). Contrary to Hoehn *et al.* (*loc. cit.*), oxidation (CrO_3, AcOH, 20°) of (**I**) gives *pregnane*-3 : 12 : 20-*trione*, m.p. 201—202° (corr.), $[\alpha]_D^{17}$ +182·1±7°, $[\alpha]_{5461}^{17}$ +218·6±8° in $COMe_2$, and not ætiocholane-3 : 12 : 17-trione. 3 : 12-*Diacetoxyætiocholanic acid*, m.p. 196—198° (corr.), prepared from (**I**) by a slight modification of the method of Hoehn *et al.* (*loc. cit.*), is hydrolysed (aq. MeOH–K_2CO_3 at 20°) to the 3(α)-*hydroxy*-12-*acetoxy*-derivative, m.p. 260—261° (corr.), energetic hydrolysis of which gives the $(OH)_2$-acid (**II**). During an attempt to degrade the carbinol from (**II**) and MgPhBr, a little of a *compound*, $C_{32}H_{38}O_3$, m.p. 200—201° (which may be diphenyl-3 : 12-diketoætiocholanylcarbinol arising from material which has resisted dehydration), was isolated. H. B.

Constituents of the adrenal cortex and related substances. XXXIV. Deoxycorticosterone and other pregnane derivatives from ætiolithocholic and 3(β)-hydroxyætiocholanic acid. T. Reichstein and H. G. Fuchs. **XXXV. Phosphoric and *p*-toluenesulphonic esters of deoxycorticosterone and related substances.** T. Reichstein and W. Schindler. **XXXVI. Proof of the position of the double linking in corticosterone. XXXVII. Reductive removal of the 21-hydroxyl group of corticosterone and analogous ketols.** T. Reichstein and H. G. Fuchs (*Helv. Chim. Acta*, 1940, **23**, 658—669, 669—675, 676—683, 684—688).—XXXIV. Me 3-keto-Δ^4-ætiocholenate is reduced (H_2, PtO_2, AcOH, 20°) to Me ætiolithocholate (**I**), m.p. 142—144° (with a little Me ætiocholanate), and *Me* 3(β)-*hydroxyætiocholanate* (**II**), m.p. 133—135°, $[\alpha]_D^{15}$ +57·2±4°, $[\alpha]_{5461}^{15}$ +68·2±3° in $COMe_2$ (*acetate*, m.p. 125—126°, $[\alpha]_D^{15}$ +54±3°, $[\alpha]_{5461}^{15}$ +63·9±5° in $COMe_2$), which may be contaminated with a little of its *allo*-isomeride; (**II**) is pptd. by digitonin whereas (**I**) is not. Oxidation (CrO_3, AcOH, room temp.) of (**I**) or (**II**) gives Me 3-ketoætiocholanate. Hydrolysis (aq. MeOH–KOH) of (**II**) affords the OH-acid, m.p. 220—225° (corr.) after a transformation at 200° (acetate, m.p. 162—174°). Acetylætiolithocholyl chloride (prep. by $SOCl_2$ at 0—20°) and CH_2N_2 in C_6H_6–Et_2O at −15° to 20° give the acetate, m.p. 76—84° (decomp.), hydrolysed by MeOH–KOH at 20°, of 21-diazopregnan-3(α)-ol-20-one, m.p. 174—178° (decomp.); the latter is converted by AcOH at 95° into *pregnane*-3(α) : 21-*diol*-20-*one* 21-*acetate* (**III**), m.p. 179·5—181° (corr.), $[\alpha]_D^{18}$ +109·4±2°, $[\alpha]_{5461}^{18}$ +136·1±2° in $CHCl_3$, and by Et_2O–HCl into 21-chloropregnan-3(α)-ol-20-one (**IV**), m.p. 95—100°. Oxidation (CrO_3, AcOH, room temp.) of (**III**) and (**IV**) affords 21-*acetoxypregnane*-3 : 20-

dione (**V**), m.p. 150—151° (corr.), $[\alpha]_D^{17}$ +109±4°, $[\alpha]_{5461}^{17}$ +130·4±4° in $COMe_2$, and 21-*chloropregnane*-3 : 20-*dione*, m.p. 185—189° (corr.) [with AcOH–KOAc at 150° (bath) gives (**V**)], respectively. Br–AcOH and (**V**) yield a compound, m.p. 165—172° (decomp.), converted by boiling C_5H_5N into deoxycorticosterone acetate. 3(*β*)-Acetoxyætiocholanyl chloride similarly gives 21-diazopregnan-3(*β*)-ol-20-one, m.p. 128—132° (decomp.) (acetate, non-cryst.), and thence 21-*acetoxypregnan*-3(*β*)-*ol*-20-*one* (+0·5H_2O), m.p. 119—123° and, in many cases, 136—138°, also oxidised to (**V**). 21-Chloro-, m.p. 157—159° (corr.), and 21-bromo-, m.p. 144—145·5° (corr.), -*allo*pregnan-3(*β*)-ol-20-one [from the diazo-compound (A., 1939, II, 552) and Et_2O–HHal] are oxidised (CrO_3, AcOH, room temp.) to 21-*chloro*-, m.p. 186—194° (corr.), and 21-*bromo*-, m.p. 177—179° (corr.), -allo*pregnane*-3 : 20-*dione*, respectively.

XXXV. The *p*-toluenesulphonates of deoxycorticosterone and other pregnane derivatives containing the ·CO·CH_2·OH side-chain cannot be prepared (in a pure condition; cf. below) using *p*-C_6H_4Me·SO_2Cl in C_5H_5N at room temp. 21-Diazo-Δ^5-pregnen-3-ol-20-one acetate (A., 1937, II, 507) and anhyd. *p*-C_6H_4Me·SO_3H in C_6H_6 at room temp. and then at 45—50° give Δ^5-*pregnene*-3 : 21-*diol*-20-*one* 21-p-*toluenesulphonate* 3-*acetate* (**VI**), m.p. 120—121°, which reacts (slowly at room temp. and rapidly when heated) with C_5H_5N forming the pyridinium *p*-toluenesulphonate, m.p. 228° (corr.; decomp.). Δ^5-Pregnene-3 : 21-diol-20-one 21-*p*-toluenesulphonate (**VII**), m.p. 123—124° [acetylated to (**VI**)], and Δ^4-*pregnen*-21-*ol*-3 : 20-*dione* p-*toluenesulphonate*, m.p. 170—171° (corr.) [from 21-diazoprogesterone (**VIII**)], are similarly prepared. (**VII**) is unaffected by aq. MeOH–$KHCO_3$ at 20° but aq. MeOH–K_2CO_3 at 20° followed by Ac_2O–C_5H_5N at 20° give Δ^5-pregnene-3 : 21-diol-20-one diacetate, m.p. 163° (corr.). With NaI and NMe_4Cl in $COMe_2$, (**VI**) affords 21-*iodo*-, m.p. 129—131°, and and 21-chloro-, m.p. 155—156° (corr.), -Δ^5-pregnen-3-ol-20-one acetate, respectively, whilst (**VII**) and MeOH–NaBr give some 21-bromo-Δ^5-pregnen-3-ol-20-one, m.p. 149—151°. Anhyd. H_3PO_4 and (**VIII**) in anhyd. dioxan at 45—50° afford deoxycorticosterone-21-phosphoric acid (the *Na* salt possesses about the same biological activity as deoxycorticosterone).

XXXVI. Oxidation (aq. MeOH–HIO_4) of dehydrocorticosterone, m.p. 170—180° (corr.), gives a little neutral product and (mainly) 3 : 11-diketo-Δ^4-ætiocholenic acid, the Me ester of which with O_3 in $CHCl_3$ at 0° followed by Zn dust and aq. AcOH affords mainly *Me* 4 : 6-*diketo*-2 : 5-*dimethyl*-5-*β*-*carboxyethyl*-1 : 2-*trimethylenedecahydronaphthalene*-3′-*carboxylate* (*A*), m.p. 165—170° (corr.). Clemmensen reduction of this gives a mixture of products from which a small amount of the dianilide of (**IX**) (below) can be prepared.



(*A*.)

Me 3-keto-Δ^4-ætiocholenate is similarly oxidised to *Me* 6-*keto*-2 : 5-*dimethyl*-5-*β*-*carboxyethyl*-1 : 2-*trimethylenedecahydronaphthalene*-3′-*carboxylate*, m.p. 159—161° (corr.), $[\alpha]_D^{17}$ +77±2° in $COMe_2$, reduced (Clemmensen) to 2 : 5-*dimethyl*-5-*β*-*carboxyethyl*-1 : 2-*trimethylenedecahydronaphthalene*-3′-*carboxylic acid* (**IX**), m.p. 263—266° (corr.), $[\alpha]_D^{17}$ +53·7±4° in $COMe_2$ [Me ester, m.p. 65—68°; *dianilide*, m.p. 177—179° (corr.), $[\alpha]_D^{17}$ +82·8±4°, $[\alpha]_{5461}^{11}$ +110·4±4° in $COMe_2$]. These results indicate that corticosterone contains a 4 : 5-double linking. Progesterone is similarly ozonised to *β*-6-*keto*-3′-*acetyl*-2 : 5-*dimethyl*-1 : 2-*trimethylenedecahydro*-5-*naphthylpropionic acid*, m.p. 173—175° (corr.), $[\alpha]_D^{17}$ +108±3° in $COMe_2$, reduced (Clemmensen) to *β*-2 : 5-*dimethyl*-3′-*ethyl*-1 : 2-*trimethylenedecahydro*-5-*naphthylpropionic acid*, begins to melt at 126° and then resolidifies with m.p. 141—145° (corr.), $[\alpha]_D^{15}$ +8·6±1·5° in $CHCl_3$.

XXXVII. Deoxycorticosterone, *p*-C_6H_4Me·SO_2Cl (2 equivs.), and C_5H_5N (3 equivs.; 10 vol.-%) in $CHCl_3$ (90 vol.-%) at room temp. give a mixture (*B*) of deoxycorticosterone *p*-toluenesulphonate and 21-chloroprogesterone; (*B*) with NaI–$COMe_2$ followed by Zn dust–AcOH affords progesterone (**X**) in good yield. Corticosterone similarly yields a mixture (*C*) of its 21-*p*-toluenesulphonate and chloride; (*C*) is converted (as above) into 11-*hydroxyprogesterone* (**XI**), m.p. 187—188° (corr.), $[\alpha]_D^{17}$ +222·5±4° in $COMe_2$, which is oxidised (CrO_3, AcOH, 20°) to 11-*ketoprogesterone*, m.p. 172—174° (corr.), $[\alpha]_D^{17}$ +238·5±8° in $COMe_2$. (**XI**) is at least 6 times less active biologically than (**X**). H. B.

Steroids. XXVI. [Preparation of] 21-acetoxy- and 21-acetoxy*allo*-pregnane-3 : 20-dione by hydrogenation of deoxycorticosterone acetate. A. Wettstein and F. Hunziker (*Helv. Chim. Acta*, 1940, **23**, 764—768).—Reduction (H_2, Pd–$CaCO_3$, EtOH) of deoxycorticosterone acetate and acetylation (Ac_2O, C_5H_5N, room temp.) of the product gives 21-acetoxy*allo*-, m.p. 197—199° (*dioxime*, decomp. 212—214°) and (mainly) 21-acetoxy-pregnane-3 : 20-dione. H. B.

Synthesis of 2-phytyl-1 : 4-naphthaquinone. P. Karrer, A. Geiger, A. Ruegger, and G. Schwab (*Helv. Chim. Acta*, 1940, **23**, 585—590).—Partly a more detailed account of work previously reviewed (A., 1940, II, 17). 2-$C_{10}H_7$·$[CH_2]_2$·OH, m.p. 67° [from 2-$C_{10}H_7$·MgBr and $(CH_2)_2O$ in 45% yield], and PBr_3 in boiling C_6H_6 give the *bromide*, b.p. 138—141°/0·3 mm., which with Mg followed by *ζκξ*-trimethylpentadecan-*β*-one affords *αδ*-*di*-2-*naphthylbutane*, m.p. 155—156°, and 2-*γ*-*hydroxy*-*γηλο*-*tetramethylhexadecylnaphthalene* (**I**). $SOCl_2$ and (**I**) give the 2-*γ*-*Cl*-derivative, which with C_5H_5N at 125° affords 2-*phytylnaphthalene*, b.p. 180—190°/0·15 mm., converted (cf. *loc. cit.*) into 2-*phytyl*-1 : 4-*naphthaquinone* which may not be homogeneous. H. B.

Preparation of anthraquinone by oxidation of anthracene with chlorine in aqueous suspension.—See B., 1941, II, 105.

Vitamin-*K* activity and structure.—See A., 1941, III, 377.

Structure of gossypol. XXIV. Attempts to prepare des*apo*gossypolone tetramethyl ether. R. Adams, T. A. Geissman, B. R. Baker, and H. M. Teeter. **XXV. Synthesis of des*apo*gossypolone tetramethyl ether.** R. Adams and B. R. Baker (*J. Amer. Chem. Soc.*, 1941, **63**, 528—534, 535—537; cf. A., 1939, II, 508).—XXIV. Prep. of 3 : 4 : 1-$(OMe)_2C_6H_3$·COEt is improved. Reduction of crude 3 : 4 : 1-$(OMe)_2C_6H_3$·CO·CHMe·CH_2·CO_2H by Zn–Hg–HCl–PhMe and subsequent methylation (Me_2SO_4–NaOH) gives *Me* *γ*-3 : 4-*dimethoxyphenyl*-*β*-*methylbutyrate*, b.p. 171—172°/2 mm. (corresponding *p*-C_6H_4Br·*CO*·CH_2 ester, m.p. 69—71°). The oily *α*-HCO-derivative, obtained therefrom by NaOEt–Et_2O–HCO_2Et at 0° (later, room temp.), is cyclised by H_2SO_4–85% H_3PO_4 at −5° to −10° to give mixed esters, b.p. 205—230°/4 mm., whence KOH–H_2O–MeOH yields 6 : 7-*dimethoxy*-3-*methyl*-3 : 4-*dihydro*-2-*naphthoic acid*, m.p. 198—200°, the *Me* ester, m.p. 119—120° (corr.), b.p. 193—195°/1 mm., of which with S at 235° and later 245—250° gives *Me* 6 : 7-*dimethoxy*-3-*methyl*-2-*naphthoate*, m.p. 126—127° (corr.) [free *acid*, m.p. 224—225° (corr.)]; this with N_2H_4,H_2O in boiling MeOH gives the *hydrazide*, m.p. 226—228° (corr.), and thence by HCl–abs. EtOH–EtO·NO at 0° *Et* 6 : 7-*dimethoxy*-3-*methyl*-2-*naphthylcarbamate*, m.p. 177—178° (corr.), which with boiling 20% KOH–MeOH gives 6 : 7-*dimethoxy*-3-*methyl*-2-*naphthylamine*, m.p. 200—201°, converted (diazo-reaction) into 2-*iodo*-6 : 7-*dimethoxy*-3-*methylnaphthalene* (**I**), m.p. 161—162° (corr.). 3-Bromo-2-methyl-1 : 4-naphthaquinone, m.p. 151—152° (corr.), best obtained from 2-methyl-1 : 4-naphthaquinone (**II**) by Br–NaOAc–AcOH at room temp., with Zn dust and, later, NaOAc in boiling Ac_2O gives 66% of 2 : 3 : 1 : 4-$C_{10}H_4MeBr(OAc)_2$ (**III**), m.p. 209° (corr.), and with $SnCl_2$ in boiling HCl–EtOH affords 2 : 3 : 1 : 4-$C_{10}H_4MeBr(OH)_2$ (93%), m.p. >250°, and thence (by Me_2SO_4–aq. KOH–N_2) 3-*bromo*-1 : 4-*dimethoxy*-2-*methylnaphthalene* (**IV**) (69%), m.p. 84—85° (corr.). Attempts to obtain dinaphthyl derivatives from (**I**), (**III**), and (**IV**) by the Ullmann reaction and from 6 : 7-*dimethoxy*-1 : 4-*naphthaquinone* (**V**), m.p. 236—237° (corr.; decomp.) (see below), and (**II**) by quinoline in AcOH failed. Prep. of 3 : 4 : 1-$(OMe)_2C_6H_3$·CO·$[CH_2]_2$·CO_2H (Et ester, m.p. 62°), -$(OMe)_2C_6H_3$·$[CH_2]_3$·CO_2H, and 1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydronaphthalene (**VI**) is improved. S at 240—250° converts (**VI**) into 6 : 7-*dimethoxy*-1-*naphthol* (45%), m.p. 168—169° (corr.), which with Me_2SO_4–KOH–MeOH gives 1 : 6 : 7-$C_{10}H_5(OMe)_3$, m.p. 128° (corr.). 4-*Nitro*-1 : 6 : 7-*trimethoxynaphthalene* (**VII**), m.p. 170° (corr.), then obtained in 61% yield by HNO_3 (*d* 1·5) in AcOH at <20°, with *p*-SO_3H·C_6H_4·N_2Cl gives a dye, reduced by $SnCl_2$–HCl to an aminonaphthol, which with $K_2Cr_2O_7$–H_2SO_4 yields (**V**) (41%), also obtained in 32% yield from (**VII**) by H_2–Raney Ni in $COMe_2$ at 2—3 atm., followed by $K_2Cr_2O_7$–H_2SO_4. Zn dust–NaOAc–Ac_2O converts (**V**) into 1 : 4-*diacetoxy*-6 : 7-*dimethoxynaphthalene*, m.p. 185° (corr.).

XXV. Presence of the dinaphthyl nucleus in gossypol is confirmed by synthesis of des*apo*gossypolone Me_4 ether (**VIII**). (2 : 6 : 1-OMe·C_6H_3Me·)$_2$ and 48% HBr in boiling AcOH yield (2 : 6 : 1-OH·C_6H_3Me)$_2$ (76%), m.p. 160—163° (corr.) (lit. 164°,

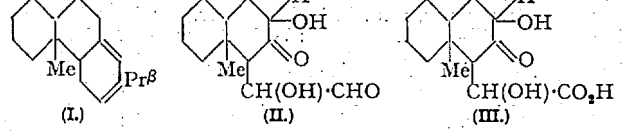
161—163·5°), which by consecutively coupling with *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$-aq. NaOH, reduction by $Na_2S_2O_4$–NaOH at 100°, and oxidation by $K_2Cr_2O_7$–H_2SO_4 at 3—5° affords 6 : 6′-*dimethyldiphenyl*-2 : 5 : 2′ : 5′-*diquinone*, m.p. 169—170° (corr.). With $(CH_2{:}C{\cdot}OMe)_2$ at 100° this gives a gummy adduct, oxidised by chloranil in boiling xylene to 6 : 7 : 6′ : 7′-tetramethoxy-3 : 3′-dimethyl-2 : 2′-dinaphthyl-1 : 4 : 1′ : 4′-diquinone [=(**VIII**)], m.p. 245—248° (uncorr.), 251—254° (corr.) [diquinol tetra-acetate, m.p. 264—265° (uncorr.), 272—273° (corr.)]. R. S. C.

III.—TERPENES.

Synthesis of *epi-iso*fenchone from *iso*fenchonequinone. A. K. Rushentzeva and N. M. Delektorskaja (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 41—43; cf. Nyman, A., 1939, II, 121).—*l-iso*Fenchone with SeO_2 in Ac_2O yields 1-1 : 2-*diketo*-3 : 5 : 5-*trimethyl*-3 : 6-endo*methylene*cyclo*hexane* (*isofenchoquinone*), m.p. 69—70°, $[\alpha]_D$ −12·64° (*oxime*, m.p. 138·5—139·4°; *semicarbazone*, m.p. 165—166°; *phenylhydrazone*, m.p. 125—126°; *NaHSO*$_3$ compound) (cf. Adler *et al.*, A., 1936, 1384), oxidised (HNO_3) to *iso*fenchocamphoric acid and reduced (Zn, AcOH) to isomerides of *hydroxyisofenchone*, m.p. 114—115° and 50—53°, $[\alpha]_D$ −31·2° and +32·4°, respectively, which are both reduced (Na, Hg) to d-epi-iso*fenchone*, b.p. 194—196°, $[\alpha]_D$ +13·6° [*oxime*, liquid (*Bz* derivative, m.p. 76—78°); *semicarbazone*, m.p. 219—220°]. One of the isomerides had been expected to give *d-iso*fenchone. F. R. G.

Application of the diene synthesis to terpenoid compounds. II. Esters derived from some maleic anhydride adducts. T. F. West (*J.C.S.*, 1941, 140—143).—With HCl–MeOH, the maleic anhydride (**I**) adducts from $\Delta^{1:3}$-*cyclo*hexadiene, myrcene, and anthracene give Me_2 esters, m.p. 69—71°, b.p. 176—178°/3 mm., and m.p. 151°, respectively, whilst the *cyclo*pentadiene adduct affords a *Me lactonic ester*, m.p. 83—84° (*acid*, m.p. 203—204°). The reaction lends support to the suggestion of Goodway *et al.* (A., 1940, II, 255) that the α-terpinene–(**I**) adduct is derived from a mixture of terpenes. F. R. S.

Resinic acids of conifers. IV. Structure of *l*-pimaric acid. S. S. Malevskaja (*J. Appl. Chem. Russ.*, 1940, **13**, 1085—1097).—*l*-Pimaric acid (**I**) yields additive *compounds* with maleic anhydride, m.p. 226—227°, and with *p*-benzoquinone, m.p. 194°; hence conjugated double linkings are present.



With O_3 (**I**) yields a *diozonide*, $C_{22}H_{30}O_8$, distilled with steam to afford $Pr^{\beta}CO_2H$ and AcOH, together with the *acid* (**II**), an oil, which solidifies on exposure to air, giving the *acid* (**III**). R. T.

Nitration of sulphodehydroabietic acid. T. Hasselstrom and S. Hopkins, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 421—422).—Sulphodehydroabietic acid and HNO_3 (*d* 1·49) at 0—5° give a $(NO_2)_1$-acid (**I**), $C_{20}H_{27}O_7NS$, m.p. >300° (cf. Fieser *et al.*, A., 1939, II, 30), and a little (?) $(NO_2)_2$-acid. The Na salt of (**I**) with boiling R_2SO_4 gives the Et_2, m.p. 195·8—196° (corr.), and Me_2 ester, m.p. 244·3—244·7° (corr.), and with Zn dust (activated by $CuSO_4$) in boiling aq. HCl–MeOH gives *aminosulphodehydroabietic acid*, m.p. >300°. R. S. C.

Saponins and sapogenins. XVI. Properties of echinocystic acid and the diketomethyl ester derived from it. J. F. Carson and C. R. Noller (*J. Amer. Chem. Soc.*, 1941, **63**, 621; cf. A., 1940, II, 311).—Data of Bergsteinsson *et al.* (A., 1934, 896) are confirmed (cf. Elliott *et al.*, A., 1940, II, 257). R. S. C.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Constituent of *Fomes officinalis*, Fris. T. Kaiyone and G. Kurono (*J. Pharm. Soc. Japan*, 1940, **60**, 110—111).—Two samples from Sakhalin and Nikko-Hondo are shown to contain agaric and *eburikoic acid* (**I**), $C_{30}H_{48}O_5$, m.p. 283°. (**I**) contains one double linking and gives a pale yellow colour with $MeNO_2$. Its *Me* ester (**II**), m.p. 141°, $[\alpha]_D^{21}$ +37·2°, is not hydrolysed by boiling KOH–EtOH. (**I**) is converted by Ac_2O in C_5H_5N into *acetyleburikoic acid*, m.p. 240°, $[\alpha]_D^{17}$ +80°; its *Me* ester, prepared by acetylation of (**II**), has m.p. 150°, $[\alpha]_D^{22}$ +56·9°. H. W.

Products of hydrogenation of lignin. H. Adkins, R. L. Frank, and E. S. Bloom (*J. Amer. Chem. Soc.*, 1941, **63**, 549—555).—" Soda lignin " (from mixed hardwoods) differs markedly from " methanol lignin " (from fresh aspen) as regards hydrogenation (Cu chromite in dioxan at 290°). The latter gives mainly (75%) C_9-units. The former gives a little *cyclo*hexanol, 4-methyl-, 4-ethyl-, and traces of 4-*n*-propyl-*cyclo*hexanol, and possibly 4-γ-hydroxy-*n*-propyl*cyclo*hexanol, but the main products are colourless oils containing up to 70 C per mol. This last result follows from analysis and determination of mol. wt. It is confirmed by Clemmensen reduction or dehydration by $H_2C_2O_4$ followed, in both cases, by hydrogenation (Raney Ni), whereby most, but not all, of the O is removed. The " methanol " and " soda " lignins contain 1 O per 6 and 13·5 C, respectively (averages). It is concluded that cyclisation occurs during treatment of the lignin with soda, that hydrogenation of the soda lignin results in saturation of the rings and fission of subsidiary O linkings, and that fission of O linkings of methanol lignin by hydrogenation leads to disruption of the mol. into C_9 units. R. S. C.

V.—HETEROCYCLIC.

Additional lower homologue of α-tocopherol. P. Karrer and K. S. Yap (*Helv. Chim. Acta*, 1940, **23**, 581—584).—γη-Dimethyl-Δ$^{\alpha}$-octinen-γ-ol, b.p. 74—80°/1 mm. (from $CHMe_2{\cdot}[CH_2]_3{\cdot}COMe$, C_2H_2, and $NaNH_2$ in Et_2O), is partially reduced (H_2, Pt, EtOH) to γη-dimethyl-Δ$^{\alpha}$-octen-γ-ol, b.p. 71—75°/12 mm., which with PBr_3 in light petroleum at <−5° and then at 15° in CO_2 gives α-bromo-γη-dimethyl-Δ$^{\beta}$-octene. This and trimethylquinol in boiling C_6H_6 + $ZnCl_2$ and N_2 afford 6-*hydroxy*-2 : 5 : 7 : 8-*tetramethyl*-2-δ-*methylamylchroman* (*allophanate*, m.p. 201°), which has no vitamin-*E* activity in 40-mg. doses. The conclusions of Evans *et al.* (A., 1940, III, 54) on the activity of various chromans etc. are criticised. H. B.

dl-**α-Tocopheryl acetate.**—See B., 1941, III, 108.

Reaction between quinones and metal enolates. XII. Dibromo-*m*-xyloquinone and sodiomalonic ester. L. I. Smith and D. J. Byers (*J. Amer. Chem. Soc.*, 1941, **63**, 612—617; cf. A., 1940, II, 101).—An increase in the no. of Br introduced into a methylated *p*-benzoquinone decreases the ease and generality of condensation to coumarins. 1 : 2 : 6 : 3 : 5 : 4-O:$C_6Me_2Br_2$:O (**I**) and $CHNa(CO_2Et)_2$ in dioxan (much less well in other solvents) give *Et* 5 : 7-*dibromo*-6-*hydroxy*-8-*methylcoumarin*-3-*carboxylate* (**II**) (44%), m.p. 192—193° (and other products) (*acetate*, m.p. 183·5—184°), hydrolysed by boiling 1 : 1 : 1 conc. HCl–$COMe_2$–H_2O to the *acid*, m.p 260—260·5° (decomp.) (*acetate*, m.p. 209·5—210°). H_2–Pd at 3 atm. reduces (**I**) in 95% EtOH to *Et* 6-*hydroxy*-8-*methyl*-3 : 4-*dihydrocoumarin*-3-*carboxylate*, m.p. 133—134°, which with HCl–$COMe_2$–H_2O in N_2 gives 6-*hydroxy*-8-*methyl*-3 : 4-*dihydrocoumarin*, m.p. 149—150°. Addition of aq. NaOH to (**II**) and Me_2SO_4 in hot MeOH and subsequent hydrolysis gives 4 : 6-*dibromo*-2 : 5-*dimethoxy*-3-*methylbenzylidenemalonic* (**III**) (71%), m.p. 208—208·5° (decomp.), and a little 5 : 7-*dibromo*-6-*methoxy*-8-*methylcoumarin*-3-*carboxylic acid*, m.p. 206—207° (*Me* ester, m.p. 170—171°); under other conditions the Me_2 ester (**IV**), m.p. 93—94°, of (**III**) is obtained. Hydrogenation (Pd; 38 lb.; EtOH) of (**III**) gives 4 : 6-*dibromo*-2 : 5-*dimethoxy*-3-*methylbenzylmalonic acid* (**V**), m.p. 151—152° (decomp.), the Me_2 ester, m.p. 92·5—94°, of which is similarly obtained from (**IV**). 2 : 6 : 3 : 5 : 1 : 4-$C_6Me_2Br_2(OMe)_2$, m.p. 114—115° (lit. 116°), with SO_2Cl_2 and a little Bz_2O_2 in boiling $CHCl_3$ gives 4 : 6-*dibromo*-2 : 5-*dimethoxy*-3-*methylbenzyl chloride*, m.p. 96—96·5°, and thence by $CHNa(CO_2Et)_2$ in EtOH (**V**). 1 : 2 : 3 : 5 : 4-O:C_6HMeBr_2:O (**VI**) (prep. from 3 : 2 : 4 : 6 : 1-$C_6HMeBr_3{\cdot}OH$ by CrO_3–AcOH at 70—75°), m.p. 114—115°, with Zn dust in aq. AcOH gives 2 : 3 : 5 : 1 : 4-$C_6HMeBr_2(OH)_2$ (**VII**), m.p. 148° (decomp.), the Me_2 ether, m.p. 71—72°, of which does not react with HCl–CH_2O. (**VII**) does not react with $Zn(CN)_2$–KCl–$AlCl_3$–Et_2O. Reduc-

tion of (VI) by $SnCl_2$–HCl–AcOH gives a product, m.p. 143—145° (decomp.) (Me ether, m.p. 60·5—61·5°). R. S. C.

Japanese *Alpinia* group. VII. Constitution of alpinetin, a constituent of the seeds of *A. chinensis*. Y. Kimura (*J. Pharm. Soc. Japan*, 1940, **60**, 87—89).—The crystals which separate from the Et_2O extract of the seeds are separated by PhMe into the freely sol. izalpinin, m.p. 195° (yield ~0·18%), and the sparingly sol. *alpinetin* [*5-hydroxy-7-methoxyflavanone*] (I), m.p. 223° (yield 0·0067%). (I) is not methylated by CH_2N_2 but is transformed by Me_2SO_4 and alkali into the Me ether, identical with synthetic 5 : 7-dimethoxyflavanone, m.p. 143° (lit. 140°). H. W.

Osage orange pigments. V. Isomerisation. M. L. Wolfrom, F. L. Benton, A. S. Gregory, W. W. Hess, J. E. Mahan, and P. W. Morgan (*J. Amer. Chem. Soc.*, 1941, **63**, 422—426; cf. A., 1940, II, 313).—The following and known facts indicate that osajin (I) and pomiferin (II) are, respectively, 5 : 4′-di- and 5 : 3′ : 4′-tri-hydroxy*iso*flavanones, containing also $C_{10}H_{15}O$ in which are one ring and two ethylenic linkings. Formation of the *iso*-compounds involves further ring-formation between the OH in positions 5 and an ethylenic linking (probably in a side-chain) of the $C_{10}H_{15}O$. With Me_2SO_4–NaOEt in boiling EtOH–$COMe_2$ or CH_2N_2 (excess) in dioxan, (I) gives a *Me*$_1$ *ether* (III), m.p. 134—135° (*acetate*, m.p. 140—140·5°, prepared by boiling NaOAc–Ac_2O but not by Ac_2O–C_5H_5N at 0°). Dihydro-osajin and H_2SO_4 in boiling AcOH give *dihydroisoosajin*, m.p. 287° (decomp.), also obtained from the acetate or diacetate by *p*-$C_5H_4Me{\cdot}SO_3H$ in boiling EtOH and converted by cold Ac_2O–C_5H_5N into the *monoacetate* (IV), m.p. 234° (unaffected by hot NaOAc–Ac_2O). *iso*Osajin (V) gives a *p-toluenesulphonate*, m.p. 189·5°, and with cold Ac_2O–C_5H_5N or boiling NaOAc–Ac_2O gives a *monoacetate*, m.p. 198·5°, reconverted into (V) by *p*-$C_6H_4Me{\cdot}SO_3H$–EtOH and with H_2–PtO_2–EtOH giving (IV). Me_2SO_4–KOH–H_2O–$COMe_2$ converts (V) into a *Me*$_1$ *ether*, m.p. 190—190·5°, also obtained from (III) by H_2SO_4–AcOH. Repeated treatment of (II) with CH_2N_2 in dioxan gives the Me_2 ether, which is unaffected by Ac_2O–C_5H_5N. Dihydropomiferin and H_2SO_4–AcOH give *dihydroisopomiferin*, m.p. 258—259° (decomp.) (*diacetate*, m.p. 218°, obtained also by hydrogenation of *isopomiferin diacetate*, m.p. 193°). The Me_2 ether of (II) gives similarly *isopomiferin Me*$_2$ *ether*, m.p. 180°. Tetra- and hexa-hydro-osajin and tetrahydropomiferin do not give *iso*-compounds. R. S. C.

Cannabis indica. **VI. Condensation of pulegone with alkylresorcinols. New synthesis of cannabinol and of a product with hashish activity.** R. Ghosh, A. R. Todd, and D. C. Wright (*J.C.S.*, 1941, 137—140).—Crude pulegol, orcinol, and $ZnCl_2$ in decalin give mainly 6″-*hydroxy*-2 : 2 : 5′ : 4″-*tetramethyl*-1′ : 2′ : 3′ : 4′ : 5′ : 6′-*hexahydrodibenzopyran*, b.p. 140—150°/10^{-2} mm. Similar condensation of pulegone yields a product which is dehydrogenated (Pd–C) to 6″-*hydroxy*-2 : 2 : 5′ : 4″-*tetramethyldibenzopyran*, b.p. 152°/10^{-3} mm. (p-*nitrobenzoate*, m.p. 215—216°), also obtained by dehydrogenation of 6″-acetoxy-2 : 2 : 5′ : 4″-tetramethyl-3′ : 4′ : 5′ : 6′-tetrahydrodibenzopyran. Pulegone and olivetol condense to a product (dehydrogenated to cannabinol) with the composition of a tetrahydrocannabinol and showing about half the hashish activity of this substance. F. R. S.

Derivatives of diphenylene oxide. V. Bromo-derivatives. S. Yamashiro (*Bull. Chem. Soc. Japan*, 1941, **16**, 6—15).—3 : 6-Dinitro- with HNO_3 (*d* 1·52) at room temp. yields 1 : 3 : 6- and 2 : 3 : 6-trinitro-, the latter further nitrated (hot HNO_3, *d* 1·52) to 1 : 3 : 6 : 7- and 2 : 3 : 6 : 7-tetranitro-diphenylene oxide. With Br in boiling CCl_4, diphenylene oxide gives mainly 3-bromo- and 3 : 6-dibromo-diphenylene oxide (I), whilst 2-bromo- yields 2 : 6- (II) and 2 : 7-*dibromo-diphenylene oxide* (III), m.p. 199—200° (corr.). (I) or (II) with Br in boiling AcOH yields 2 : 3 : 6-*tribromo*-, m.p. 202—203° (corr.), further brominated to 2 : 3 : 6 : 7-, m.p. 306—307° (corr.) [also obtained from (II) or (III)], and 1 : 3 : 6 : 7-*tetrabromo-diphenylene oxide*, m.p. 248—249° (corr.) [also obtained from (II)]. 3 : 6-Dibromo-1 : 8-diamino- by the diazo-reaction yields 1 : 3 : 6 : 8-*tetrabromo-diphenylene oxide*, m.p. 237—238°. A. Li.

Fluorescence, phosphorescence, and photochemistry of dyes.—See A., 1941, I, 150.

Coumaranocoumarans. J. B. Niederl and R. H. Nagel (*J. Amer. Chem. Soc.*, 1941, **63**, 580—581).—*m*-$C_6H_4(OH)_2$ (I) and Ac_2 (0·5 mol.) in AcOH, first boiling and then (2 weeks) at room temp., give 5 : 5′-*dihydroxy*-1 : 2-*dimethyl*-1 : 2-*dihydrobenzfurano*-1′ : 2′-2 : 1-*dihydrobenzfuran*, m.p. 214° (*diacetate*, m.p. 158°; *dipropionate*, m.p. 132°). Bz_2, (I), and H_2SO_4 in AcOH at room temp. (3 months) give 5 : 5′-*dihydroxy*-1 : 2-*diphenyl*-1 : 2-*dihydrobenzfurano*-1′ : 2′-2 : 1-*dihydrobenzfuran*, m.p. 254—256° (*diacetate*, m.p. 182°; *dipropionate*, m.p. 113—116°). R. S. C.

α-Coumarilyl- and α-thionaphthenoyl-acetic esters and anilides.—See B., 1941, II, 109, 132.

Derivatives of αα-diphenyl-γ-piperidinobutyric acid.—See B., 1941, III, 80.

Pyridine series. II. Synthesis of 2-methyl-3-β-hydroxyethylpyridine and of the pyridine analogue of thiamin (vitamin-B_1). A. H. Tracy and R. C. Elderfield (*J. Org. Chem.*, 1941, **6**, 54—62; cf. A., 1939, II, 560).—Et α-β′-ethoxyethylacetoacetate, b.p. 113—117°/10 mm., obtained in 56% yield from $CH_2Ac{\cdot}CO_2Et$ and $OEt{\cdot}[CH_2]_2{\cdot}Br$ in dioxan, is converted into *Et β-amino-α-β′-ethoxyethylcrotonate* (I), b.p. 96·5—98·5°/0·4 mm., m.p. 13—14°, by saturation with NH_3 in presence of NH_4NO_3 at 0° and subsequent heating at 65° for 4 hr. and then at 65—70° for 3 hr. It is converted by NaOEt and $CH_2(CO_2Et)_2$ at 145—150° (8 hr.) into *Et* 4 : 6-*dihydroxy*-2-*methyl*-3-β-*ethoxyethylpyridine*-5-*carboxylate* (II), m.p. 174—176° [*dioxime*, m.p. 240—242° (decomp.)], which gives an orange-red colour with $FeCl_3$. Treatment of (II) with boiling 10% NaOH followed by boiling 10% HCl leads to 4 : 6-*dihydroxy*-2-*methyl*-3-β-*ethoxyethylpyridine*, m.p. 290—293° (block; decomp.), transformed by boiling $POCl_3$ into 4 : 6-*dichloro*-2-*methyl*-3-β-*ethoxyethylpyridine*, b.p. 98—99°/0·4 mm. This is dechlorinated by H_2 in MeOH containing KOAc and Pd-black to 2-*methyl*-3-β-*ethoxyethylpyridine*, b.p. 72—73°/0·5 mm. [*picrate*, m.p. 63—64°; *platinichloride*, m.p. 165—168° (decomp.); *aurichloride*, m.p. 108—109°], converted by conc. HCl at 150° into 2-*methyl*-3-β-*chloroethylpyridine* [*picrate*, m.p. 134—135°; *platinichloride*, m.p. 189—190° (decomp.); *aurichloride*, m.p. 116—117°], which with H_2O at 160° gives 2-*methyl*-3-β-*hydroxyethylpyridine monohydrate* (III), b.p. 120—125°/0·5 mm., m.p. 61—62° (*picrate*, m.p. 123—124°; hygroscopic *methiodide*, m.p. 103—104°; p-*nitrobenzoate*, m.p. 114—115°), oxidised by alkaline $KMnO_4$ to quinolinic acid. (III) and 4-amino-2-methyl-5-bromomethylpyrimidine hydrobromide in light petrolatum at 100° afford 2-*methyl*-1-4′-*amino*-2′-*methyl*-5′-*pyrimidylmethyl*-3-β-*hydroxyethylpyridinium bromide hydrobromide*, chars at 240—260°. Details are given of the prep. of Et β-acetamidocrotonate (IV), m.p. 63—65°, from $CH_2Ac{\cdot}CO_2Et$, NH_2Ac, and $AlCl_3$. *Et β-acetamido-α-β′-ethoxyethylcrotonate* (V), b.p. 118—120°/0·5 mm., is best obtained by direct acetylation of (I). Ring-closure of (IV) or (V) could not be effected by Na in PhMe or dioxan or by treating with NaOEt. Successive additions of Et α-β′-ethoxyethylacetoacetate and $Br{\cdot}[CH_2]_2{\cdot}CO_2Et$ to Na in Et_2O give *Et*$_2$ *α-acetyl-α-β′-ethoxyethylglutarate*, b.p. 133—136°/1 mm., which gave unworkable products under the influence of hot or cold dil. acid or alkali. M.p. are corr. H. W.

Pyridine series. III. Synthesis of 2 : 3-dialkylpyridines from α-formyl ketones. A. H. Tracy and R. C. Elderfield (*J. Org. Chem.*, 1941, **6**, 63—69).—Condensation of γ-formylbutan-β-one (I), from $COMeEt$, HCO_2Et, and Na in anhyd. Et_2O, with $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ in abs. EtOH containing piperidine gives a compound regarded as 3-*cyano*-4-*hydroxy*-5 : 6-*dimethyldihydro*-2-*pyridone* (II), m.p. 347° (block; decomp.), since it readily gives an *acetate*, m.p. 283—285° (decomp.). (II) is hydrolysed by conc. HCl to 5 : 6-*dimethyl*-2-*pyridone*-3-*carboxylic acid*, m.p. 310—312° (block; decomp.), decarboxylated at 325—335° to 2-*hydroxy*-5 : 6-*dimethylpyridine*, m.p. 208—209°. This is transformed by $POCl_3$ and PCl_5 into 2-*chloro*-5 : 6-*dimethylpyridine*, b.p. 100—101°/11 mm.; m.p. 10—11° (*picrate*, m.p. 120·5—121°), which is converted by H_2–Pd-black in EtOH into 2 : 3-dimethylpyridine (II), b.p. 161—164° (picrate, m.p. 187—188°). It thus appears that (I) has the assumed constitution and that a derivative of (II) is the product of the interaction of (I) and $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ regardless of the mechanism by which the latter reaction may take place. *Me γ-ethoxypropyl ketone*, b.p. 169—172°, obtained by the hydrolysis (5% NaOH) of Et α-β′-ethoxyethylacetoacetate, condenses with HCO_2Et in presence of Na and light petroleum to *α-ethoxy-γ-formylpentan-δ-one*, b.p. 85—87°/14 mm., which polymerises so rapidly that it is

impossible to obtain accurate analytical results or to prepare CO derivatives. The crude compound is condensed with $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ to give a small yield of (?) *3-cyano-6-methyl-5-β-ethoxyethyl-2-pyridone*, m.p. 179—181°, hydrolysed by 48% HBr at 150—160° to (?) *6-methyl-5-β-bromoethyl-2-pyridone*, m.p. 258° (decomp.), in poor yield. M.p. are corr. H. W.

Pyridine series. IV. Ethyl propionylpyruvate; its condensation with phenylhydrazine and use for the synthesis of 2-ethylisonicotinic acid. A. H. Tracy and R. C. Elderfield (*J. Org. Chem.*, 1941, **6**, 70—76).—Et propionylpyruvate (**I**), which is shown to be the sole product of the action of COMeEt and $Et_2C_2O_4$, condenses with $NHPh{\cdot}NH_2$ in boiling glacial AcOH to *Et 1-phenyl-3*(or 5)*-ethylpyrazole-5*(or 3)*-carboxylate*, b.p. 125—127°/0·3 mm., and 152—154°/0·3 mm.; the corresponding *acids*, m.p. 135—136° and 140—141°, respectively are oxidised by alkaline $KMnO_4$ to 1-phenylpyrazole-3 : 5-dicarboxylic acid, m.p. 270—272° (decomp.) (Me_2 ester, m.p. 124—125°). (**I**) is condensed with $CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ by piperidine in EtOH at 60° to *Et 3-cyano-6-ethyl-2-pyridone-4-carboxylate*, m.p. 217—218° (decomp.), converted by boiling conc. HCl into *6-ethyl-2-pyridone-4-carboxylic acid* (**II**), m.p. 308° (block; decomp.); this could not be decarboxylated by the customary methods but is transformed by CH_2N_2 into *Me 2-methoxy-6-ethylpyridine-4-carboxylate* (*picrate*, m.p. 133—135°). (**II**) and $POCl_3$–PCl_5 at 125—149° afford, after treatment with warm 5% NaOH, *2-chloro-6-ethylpyridine-4-carboxylic acid*, m.p. 136—137°, which is transformed (H_2–Pd-black–AcOH) into *2-ethylisonicotinic acid*, m.p. 233—235°; this could not be successfully decarboxylated but is oxidised by alkaline $KMnO_4$ to pyridine-2 : 4-dicarboxylic acid, m.p. 247—249°. M.p. are corr. H. W.

Sulphanilamide compounds. VI. N^4-Acyl-N^1-heterocyclic and N^1-heterocyclic sulphanilamides. H. G. Kolloff and J. H. Hunter (*J. Amer. Chem. Soc.*, 1941, **63**, 490—492; cf. A., 1941, II, 66).—Picolinic (prep. from 2-picoline), nicotinic, and *iso*nicotinic acid [prep. from 4-picoline, b.p. 141—142° (purified as oxalate, m.p. 139—140°)] with H_2SO_4–EtOH give the Et esters (*A*), which are used for the following reactions. (*A*) + aq. NH_3 at room temp. → $C_5H_4N{\cdot}CO{\cdot}NH_2$ → (+ P_2O_5) $C_5H_4N{\cdot}CN$ (*B*) → (+ H_2–Raney Ni; aq. NH_3–EtOH; room temp./4 atm.) 2- (38·2%), b.p. 90—93°/3 mm. (? 75—76°/2—3 mm.) [*p*-nitrobenzoate (? *p*-$NO_2{\cdot}C_6H_4{\cdot}CO$ derivative), m.p. 137—138°], 3- (60·1%), b.p. 95—98° (? 115—116°)/? mm. [*p*-nitrobenzoate (? *p*-$NO_2{\cdot}C_6H_4{\cdot}CO$ derivative), m.p. 190—191°], and 4-pyridylmethylamine, b.p. 115·5—117°/5 mm. (Bz derivative, an oil); (*A*) + EtOAc + NaOEt → $C_5H_4N{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ → (+HCl) 2- (50·4%), b.p. 187—190°, 3- (81%), b.p. 217—218°, and 4-pyridyl Me ketone (79·5%), b.p. 211—212° [also obtained less well from (*B*) by MgMeI etc.] → oximes → (+ H_2–Raney Ni) α-2- (65·1%), b.p. 194—196°, α-3- (53·3%), b.p. 216—219°, and α-4-pyridylethylamine (65·6%), b.p. 221—223° (picrate, m.p. 159—160°). Condensation of the primary amines with *p*-$NHAcyl{\cdot}C_6H_4{\cdot}SO_2Cl$ is effected in $COMe_2$–C_5H_5N or dioxan, and the product is hydrolysed by HCl–EtOH or aq. NaOH, the following being prepared: N^4-acetyl-N^1-2-pyridyl-, m.p. 224—226°, *-2-pyridylmethyl-*, m.p. 124—125°, *-α-2-pyridylethyl-*, m.p. 142—142·5°, -3-pyridyl-, m.p. 280°, *-3-pyridylmethyl-*, m.p. 181—181·5°, *-α-3-pyridylethyl-*, m.p. 249°, *-4-pyridyl-*, m.p. 256—257°, *-4-pyridylmethyl-*, m.p. 196—200°, and *-α-4-pyridylethyl-*, m.p. 205°, *-sulphanilamide*. N^1-2-, m.p. 189°, N^1-3-, m.p. 256—257°, and N^1-4-pyridyl-, m.p. 235—236°, N^1-2-, m.p. 130·8—131°, N^1-3-, m.p. 133—135°, and N^1-4-*pyridylmethyl-*, m.p. 183—183·5°, N^1-α-2-, m.p. 135—136°, N^1-α-3-, m.p. 164·5—165·5°, and N^1-α-4-*pyridylethyl-*, m.p. 194—195°, *-sulphanilamide*, N^4-*n*-Hexoyl-N^1-2-pyridyl-, m.p. 200—201°, *-2-pyridylmethyl-*, m.p. 174—175°, *-α-2-pyridylethyl-*, m.p. 143·5—144°, *-3-pyridyl-*, m.p. 174—175°, *-3-pyridylmethyl-*, m.p. 97·5—99·5°, *-α-3-pyridylethyl-*, m.p. 168·5°, *-4-pyridyl-*, m.p. 222—223°, *-4-pyridylmethyl-*, m.p. 131°, and *-α-4-pyridylethyl-*, m.p. 159—160°, *-sulphanilamide*. R. S. C.

Pyridine-3-sulphon-2′-pyridylamide, m.p. 185°.—See A., 1941, III, 215.

Polarisation in heterocyclic rings with aromatic character. Polarisation in the quinoline ring. E. Ochiai and K. Kokeguchi (*J. Pharm. Soc. Japan*, 1940, **60**, 98—103).—The naphthoid character of the quinoline ring is further illustrated by the Cl-substitution of 8- or 6-hydroxyquinoline, the Skraup reaction with 6-aminoquinoline, the Bucherer reaction of hydroxyquinolines, and the coupling of aminoquinolines with PhN_2Cl. *7-Allyloxyquinoline*, b.p. 145°/4 mm. (*hydrochloride*, m.p. 178—180°; *picrate*, m.p. 188—189°), obtained by the action of allyl bromide on the derivative of 7-hydroxyquinoline (**I**) or, preferably, on (**I**) in abs. EtOH containing K_2CO_3, is isomerised at 230° to *7-hydroxy-8-allylquinoline* (**II**), m.p. 139—140°, catalytically reduced (Pd–C in MeOH) to *7-hydroxy-8-n-propylquinoline*, m.p. 169—170° (*picrate*, m.p. 156—158°; *hydriodide*, m.p. 243—245°). (**II**) is converted analogously into *7-allyloxy-8-allylquinoline*, b.p. 170° (bath)/6 mm. (*picrate*, m.p. 139—141°; *hydriodide*, m.p. 150—151°; *hydrochloride*, m.p. 164—165°), which is unchanged at 250°. Hence only one of the two positions *ortho* to $C_{(7)}$ is activated. 4 : 2 : 5 : 1-$NH_2{\cdot}C_6H_2Me_2{\cdot}OH$, H_3AsO_4, B_2O_3, and glycerol afford *6-hydroxy-5 : 8-dimethylquinoline* (**III**), m.p. 165° (*acetate*, m.p. 65°). 6- and 7- (**IV**) -Hydroxyquinoline couple with *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ in dil. AcOH to *5-p-nitrobenzeneazo-6-hydroxy-*, decomp. 274—275°, and *8-p-nitrobenzeneazo-7-hydroxy-* (**V**), m.p. 265°, *-quinoline*. Under these conditions 5-chloro-6-hydroxy- and 7-hydroxy-8-*n*-propylquinoline and (**III**) are unchanged whereas 8-bromo-7-hydroxyquinoline (**VI**) loses Br and give (**V**). (**IV**) and (**VI**) do not react with PhN_2Cl under similar conditions. H. W.

Sulphonamidoquinolines.—See B., 1941, III, 109.

Preparation of some condensation products of *m*-dialkylaminobenzaldehydes with compounds containing reactive methylene groups, and an investigation of their suitability as photographic sensitisers. W. Cocker and D. G. Turner (*J.C.S.*, 1941, 143—145).—The condensation products of 6-substituted quinaldine methiodides with *m*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ and *m*-$NEt_2{\cdot}C_6H_4{\cdot}CHO$ are described: they are of little val. as photographic sensitisers. The substances are *6-methoxyquinaldine*, m.p. 64—65°, *2-m-dimethylaminostyryl-6-methylquinoline methiodide*, m.p. 253°, *6-bromo-*, m.p. 244·5°, and *6-methoxy-2-m-dimethylaminostyrylquinoline methiodide*, m.p. 235° (decomp.), and *6-methoxy-*, m.p. 240° (decomp.), and *6-dimethylamino-2-m-diethylaminostyrylquinoline methiodide*, m.p. 220—221°. F. R. S.

Aeridine syntheses and reactions. I. Synthesis of proflavine from *m*-phenylenediamine and its derivatives. A. Albert (*J.C.S.*, 1941, 121—125).—*m*-$C_6H_4(NH_2)_2$ (1 mol.), glycerol (4 mols.), $ZnCl_2$ (1·33 mols.), and $H_2C_2O_4{,}2H_2O$ (1 mol.) at 155° for 45 min. give proflavine (**I**) (55—65% yield) and small amounts of 2 : 8 : 2′ : 8′-*tetra-amino-5 : 10-dihydrodiacridyl 5 : 5′-ether* (+$2H_2O$), decomp. 260° (efferv.) [($PrCO)_4$ derivative, m.p. 250°]. Glycerol may be replaced by alcohols which convert $H_2C_2O_4$ into CH_2O_2. $ZnCl_2$ may be replaced by $CaCl_2$ but not by $SnCl_2$ or $AlCl_3$. The yield of (**I**) falls in linear proportion when the amount of $ZnCl_2$ is decreased. If $ZnCl_2$ is omitted, the principal product is *m*-amino-oxanilic acid, but when heated with *m*-$C_6H_4(NH_2)_2$ and HCl this substance gives only 23% of (**I**). Interrupting the main reaction at 130° gives *m-aminoformanilide*, m.p. 107°, which condenses with *m*-$C_6H_4(NH_2)_2$ and HCl yields 70% of (**I**). 2 : 8-*Diform-*, m.p. 251° (decomp.) and *-dibutyramidoacridine*, m.p. 265°, are described. The mechanism of the initial stages of the reaction is discussed. F. R. S.

Problem of colour of organic compounds. F. S. Schifrin (*Compt. rend. Acad. Sci., U.R.S.S.*, 1940, **29**, 27—31).—Sklar's theory (A., 1937, I, 547) is shown to be valid for N rings but not for O or S rings. The author agrees with Förster (A., 1939, II, 399). F. R. G.

Heterocyclic nitrogen compounds. XLVIII. Synthesis of 2 : 7-phenanthroline. P. Ruggli and O. Schetty (*Helv. Chim. Acta*, 1940, **23**, 725—729).—$NH_2{\cdot}CH_2{\cdot}CH(OEt)_2$ (2·5—3·3 mols.) with *p*- and *m*-$C_6H_4(CHO)_2$ and 2 : 1 : 4-$NO_2{\cdot}C_6H_3(CHO)_2$ at 60—70° gives *terephthalylidene-* (**I**), m.p. 61°, *isophthalylidene-*, b.p. 165°/13 mm., and *nitroterephthalylidene-*, m.p. 37°, *-di-β-aminoacetal*, respectively. Reduction (H_2, Raney Ni, H_2O–EtOH–EtOAc) of (**I**) affords the non-cryst. *p*-di-(ββ-diethoxyethylaminomethyl)benzene, the hydrochloride of which with 33% oleum at +20° yields (by loss of 4 EtOH and dehydrogenation) a little 2 : 7-phenanthroline, m.p. 225° [chromate; picrate, m.p. 235°; platinichloride; *dimethiodide* (+H_2O), decomp. 258°]. H. B.

Ultra-violet absorption spectra of barbituric acid and its 1-methyl and 1 : 3-dimethyl derivatives. R. E. Stuckey (*Quart. J. Pharm.*, 1940, **13**, 312—317).—The absorption spectra of the three substances were determined in acid and alkaline solutions and at varying concn. in H_2O. Com-

mercially pure barbituric acid (I) has an absorption band at 2940—3395 A. but this disappears on repeated crystallisation of (I) from H_2O. In alkaline solution, all three substances show the almost identical val. of $\varepsilon_{max.}$ ~2600 A., indicating that (I) in aq. solution undergoes only one enolisation, viz., that involving the active CH_2 group in position 5. F. O. H.

1 : 3-Dimethyl-5-alkylbarbituric acids. A. C. Cope, (Misses) D. Heyl, D. Peck, C. Eide, and A. Arroyo (*J. Amer. Chem. Soc.*, 1941, **63**, 356—358).—1 : 3-*Dimethyl-5-ethyl-*, b.p. 130—132°/6 mm., -iso*propyl-*, m.p. 108·5—109·5°, -n-, m.p. 44—45°, and -sec.-*butyl-*, m.p. 74·5—75·5°, -iso-, m.p. 43—44°, and -sec.-*amyl-*, m.p. 55—56·5°, -cyclo*hexyl-*, m.p. 128·5—129°, and *-phenyl-barbituric acid*, m.p. 140—140·5°, and 1 : 3 : 5-*trimethylbarbituric acid*, m.p. 89·5—90°, are prepared from $CO(NHMe)_2$ with boiling $CHR(CO_2Et)_2$ and NaOEt or $CHR(CO_2H)_2$ in AcOH–Ac_2O at 60—70°, later 90°. NaOCl–HCl, followed by $SnCl_2$–HCl, converts caffeine into tetramethylalloxantine (81%), which with PCl_5 in $(CHCl_2)_2$ at 155—165° gives 5 : 5-dichloro-1 : 3-dimethylbarbituric acid (76%), m.p. 157—158°, reduced by H_2–Pd–C in $COMe_2$ at 50°/1—2 atm. to 1 : 3-dimethylbarbituric acid. With CH_2PhCl and NaOH in aq. EtOH this gives 5-*benzyl*-1 : 3-*dimethylbarbituric acid*, m.p. 116·5—117·5°, also obtained from the CHPh: compound by H_2–Pd–C in $COMe_2$. The trialkyl-acids have no useful anæsthetic properties. R. S. C.

Barbituric acids.—See B., 1941, III, 108.

Derivatives of piperazine. XIX. Reactions with arylsulphonyl chlorides and sulphonic acids. M. E. Smith and C. B. Pollard (*J. Amer. Chem. Soc.*, 1941, **63**, 630—631; cf. A., 1940, II, 141).—1 : 4-Di-benzene-, m.p. 291·3—291·7° (lit. 282—283°), *-p-*, m.p. 298·4—298·6° (lit. 286°), and -o-*toluene-*, m.p. 209·0—209·4°, -p-*bromobenzene-*, m.p. >300°, and -o-*nitrobenzene-sulphonylpiperazine*, m.p. 278—278·3°, and *piperazinium di-benzene-*, -p-*toluene-*, -2-*chloro*-5-*nitrobenzene-*, and -2 : 5-*dichlorobenzene-sulphonate*, m.p. >300°, are prepared. M.p. are corr. R. S. C.

Synthesis of a keto-derivative of glyoxaline. Preparation of 4-methylglyoxaline-5-propionic ester. Y. Tamamushi (*J. Pharm. Soc. Japan*, 1940, **60**, 92—95).—Et 4-methylglyoxaline-5-carboxylate is converted by N_2H_4,H_2O at 120° into 4-*methylglyoxaline-5-carboxhydrazide*, m.p. 220°, transformed by $PhSO_2Cl$ and C_5H_5N into the *$PhSO_2$* derivative, m.p. 227°, which gives 4-*methylglyoxaline-5-aldehyde* (I), (p-*nitrophenylhydrazone*, m.p. 275°) when heated with borax in $(CH_2{\cdot}OH)_2$ at 160°. Exposure to sunlight of (I) and $CH_2(CO_2H)_2$ in H_2O containing piperidine affords *α-carboxy*-4-*methylglyoxaline*-5-*acrylic acid*, m.p. 228°, reduced (H_2–Pd-C in MeOH) to the corresponding *propionic acid*, m.p. 210°, which is decarboxylated at 210° and then esterified (CH_2N_2 in Et_2O) to *Me* 4-*methylglyoxaline-5-propionate* (*picrate*, m.p. 138°). H. W.

Synthesis of an alkamine derivative of glyoxaline. Y. Tamamushi (*J. Pharm. Soc. Japan*, 1940, **60**, 96—98).—5-Bromoacetyl-4-methylglyoxaline and $(CH_2)_6N_4$ in $CHCl_3$ at room temp. give the additive *compound* $C_{12}H_{19}ON_6Br,HBr$, m.p. 161°, hydrolysed by HBr in aq. EtOH at room temp. to 5-aminoacetyl-4-methylglyoxaline (I) (*dipicrate*, m.p. 178°; *dihydrochloride*, m.p. 335°), which strongly reduces Fehling's solution; it is very resistant to reduction (H_2–PtO_2 or Pd–C) in acid solution and decomposes in the presence of alkali. Reduction of (I) by Na–Hg in H_2O kept neutral by addition of AcOH yields 4-methyl-5-β-amino-α-hydroxyethylglyoxaline (*dipicrate*, m.p. 157°; dihydrochloride, m.p. 210°). H. W.

Polarisation in heterocyclic rings with aromatic character. XI. Substitution of phenylglyoxalines. E. Ochiai and K. Utahashi (*J. Pharm. Soc. Japan*, 1940, **60**, 104—109).—Both aromatic rings of phenylglyoxaline are similarly and more readily nitrated than C_6H_6 or glyoxaline (I); NO_2 enters the *p*-position of Ph on 5-position of (I). 4-Phenylglyoxaline (II) is converted by a well-cooled mixture of conc. H_2SO_4 and fuming HNO_3 into the scarcely basic 5-*nitro*-4-p-*nitrophenylglyoxaline*, m.p. 285—286° (*K* salt, decomp. 289°), oxidised by $KMnO_4$ to *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$. Under like conditions but in absence of conc. H_2SO_4 (II) is nitrated to 4-p-*nitrophenylglyoxaline*, decomp. 179—180°, oxidised to *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$ and reduced (H_2–Pd–C) to 4-*p*-aminophenylglyoxaline, m.p. 91—93·5° (Ac_1 derivative, m.p. 244—246·5°). Analogous nitration of 4-methyl-2-phenylglyoxaline (III) in absence of conc. H_2SO_4 yields 5-*nitro*-2-p-*nitrophenyl*-4-*methylglyoxaline*, m.p. 248—249°, oxidised to *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$. (II) and Br in $CHCl_3$ at room temp. afford 5-*bromo*-4-*phenylglyoxaline*, m.p. 215°, oxidised to BzOH, which resists further bromination but is converted by Br in boiling AcOH into 5-*bromo*-4-p-*bromophenylglyoxaline*, m.p. 192°, oxidised to *p*-$C_6H_4Br{\cdot}CO_2H$. (II) and (III) do not undergo the Friedel–Crafts reaction. H. W.

Benziminazole. I. Mechanism of benziminazole formation from *o*-phenylenediamine. II. Preparation of 2-α-alkylaminoethylbenziminazoles. C. H. Roeder and A. R. Day (*J. Org. Chem.*, 1941, **6**, 25—35).—I. *o*-$C_6H_4(NHAc)_2$ does not give 2-methylbenziminazole (I) when heated in boiling xylene (II) or *p*-cymene (III) whereas *o*-$NH_2{\cdot}C_6H_4{\cdot}NHAc$ gives a quant. yield of (I) in boiling (II). *o*-$NH_2{\cdot}C_6H_4{\cdot}NMeAc$ when dry is stable in boiling (II) or (III), but gives a small proportion of 1 : 2-dimethylbenziminazole (IV) in boiling, moist (III), dobtless owing to partial hydrolysis. *o*-$NHMe{\cdot}C_6H_4{\cdot}NHAc$ undergoes quant. ring-closure in boiling (II) and slow ring-closure at 50—60°. In agreement with Phillips (A., 1930, 223), it is shown that the ring-closure produced by the action of org. acids on *o*-$C_6H_4(NH_2)_2$ proceeds through the monoacyl derivative which probably eliminates H_2O by losing the O of the acyl group with one H from each of the two N. *o*-$NO_2{\cdot}C_6H_4{\cdot}NHMe$ is converted by warm Ac_2O containing a trace of conc. H_2SO_4 into *o*-$NO_2{\cdot}C_6H_4{\cdot}NMeAc$, m.p. 71·2—71·4° (corr.), catalytically reduced to *o*-$NH_2{\cdot}C_6H_4{\cdot}NMeAc$, m.p. 149·9—150·3° (corr.) (lit., m.p. 67—68°). *o*-$NH_2{\cdot}C_6H_4{\cdot}NHMe$ is converted into (IV) when heated with Ac_2O in anhyd. Et_2O at room temp. but into o-*acetamido*-N-*methylaniline*, m.p. 71·5—79·5° (corr.), when Ac_2O in Et_2O is gradually added to the free base in dry Et_2O containing $NaHCO_3$.

II. In connexion with the prep. of local anæsthetics 2-α-chloroethylbenziminazole (V) has been condensed with *sec.* amines. The compounds obtained with morpholine and $NHMe_2$ are appreciably sol. in H_2O. These derivatives form only dihydrochlorides the 2% aq. solutions of which are markedly acidic (p_H ~3). With primary amines superior to NH_2Me a normal reaction takes place yielding substances which give monohydrochlorides of which the aq. solutions have p_H 6—7. Reaction with NH_2Me or NH_3 involves 2 mols. of (V). The best yields of (V) are obtained by boiling *o*-$C_6H_4(NH_2)_2$ with $CHMeCl{\cdot}CO_2H$ and 4N—6N-HCl for 3 hr. The following *-benziminazoles* are described: 2-α-*dimethylaminoethyl-*, m.p. 208—210° (decomp.) (*dihydrochloride*, m.p. 125·5—191°); 2-α-*diethylaminoethyl-*, m.p. 177·5—178° (*dihydrochloride*, m.p. 137·5—185°); 2-α-*di*-n-*butylaminoethyl-*, m.p. 139·1—139·3° (*dihydrochloride*, m.p. 132·5—175°); 2-α-*dibenzylaminoethyl-*, m.p. 222·3—223·2° (*dihydrochloride*, m.p. 183·3—208°); 2-α-*morpholinoethyl-*, m.p. 196·8—197° (*dihydrochloride*, m.p. 140—214°); 2-α-*piperidinoethyl-*, m.p. 167—167·2° (*dihydrochloride*, m.p. 168·5—215°); 2-α-*ethylaminoethyl-*, m.p. 149—149·3° (*monohydrochloride*, m.p. 225·7—226°); 2-α-n-*butylaminoethyl-*, m.p. 120·3—121·7° (*monohydrochloride*, m.p. 171·8—172·7°); 2-α-*benzylaminoethyl-*, m.p. 155·5—156° (*monohydrochloride*, m.p. 218—220°). *Di*-α-(*benziminazolylethyl*)-*amine*, m.p. 206·8—210·2° (*dihydrochloride*, m.p. 236—270°), and *-methylamine*, m.p. 205·1—205·9° (*dihydrochloride*, m.p. 234—237°), are described. M.p. are corr. The wide m.p. ranges of many dihydrochlorides are due to loss of HCl during heating. M.p. are determined with rise of temp. of ~1° per min. H. W.

Structure of the nitroindazoles and their *N*-methyl derivatives. I. M. Barclay, N. Campbell, and G. Dodds (*J.C.S.*, 1941, 113—118).—Consideration of the possible formulæ for the Me derivatives of all the 3-bromo-*x*-nitroindazoles shows that reactive Br (piperidine) will be found only in (the quinonoid form of) 3-bromo-5-nitro-2-methylindazole; experiment verifies this. Structures have been assigned as follows: 4-nitroindazole gives 1-Me, m.p. 136° (lit. 138—139°), and 2-Me derivatives, m.p. 98° (lit. 101—103°), and the former is brominated to 3-*bromo*-4-*nitro*-1-*methylindazole*, m.p. 216—220°. 3-*Bromo*-5-*nitroindazole* has m.p. 221°. 5-Nitro-1-methylindazole has m.p. 163° and is brominated to the 3-*Br*-compound, m.p. 225°; the 2-Me derivative has m.p. 129°, and is brominated to the 3-*Br*-compound, m.p. 188°. 5 : 2 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}CHO$ [2 : 4-*dinitrophenylhydrazone*, m.p. 280° (decomp.)] with $NHMe{\cdot}NH_2,H_2SO_4$ gives 2-*chloro*-5-*nitrobenzaldehydemethylhydrazone*, m.p. 121—122°, which could not be cyclised. Methylation of 3-bromo-6-nitroindazole or bromination of 6-nitromethylindazole yields 3-*bromo*-6-*nitro*-2-, m.p. 175°, and -1-*methylindazole*, m.p. 156°. p-*Nitrobenzyl* 4-, m.p. 149°, and 6-*nitro*-o-*toluate*, m.p.

108—114°, are described. The quinonoid formula for 2-alkylindazoles is suggested. There are indications that indazole resembles in structure the 1-alkyl compounds and this is confirmed by absorption spectra measurements. The validity of the Auwers rule for the alkylation of indazoles is questioned. F. R. S.

Indigosols and their adsorptive behaviour. P. Ruggli and M Staüble (*Helv. Chim. Acta*, 1940, **23**, 689—717).—Indigosols (in H_2O) are determined by pptg. the dye with $(NH_4)_2Fe_2(SO_4)_4,24H_2O$–aq. H_2SO_4 at room temp. or at 60—70°. Indigosol O (**I**) is purified by extraction with EtOH at 50—60° and pptn. by Et_2O of traces of inorg. material, to give the *trihydrate*, $C_{16}H_{10}O_8N_2S_2Na,3H_2O$, converted by P_2O_5 at 100° in vac. into the anhyd. form, or by evaporation of an aq. solution in the dark into a *tetrahydrate*. The latter affords a C_5H_5N, $C_{16}H_{12}O_8N_2S_2,2C_5H_5N$, NH_2Ph (+2NH_2Ph, anhyd. or +2H_2O), and *benzidine* salt (+$C_{12}H_{12}N$), and a $COMe_2$ *compound*, $C_{16}H_{10}O_8N_2S_2Na_2,4COMe_2$. Indigosol O4B (**II**), from 5 : 7 : 5′ : 7′-tetrabromoindigotin and Indigosolrosa IR extra (**III**), from 6 : 6′-dichloro-4 : 4′-dimethylthioindigotin, are purified and afford anhyd. forms or *hexahydrates*. (**II**) (+6H_2O) gives C_5H_5N salts (+4 and +2C_5H_5N) and an NH_2Ph (+2NH_2Ph), and *benzidine* salt (+$C_{12}H_{12}N$). (**III**) (+6H_2O) yields a C_5H_5N, $C_{16}H_{12}O_8Cl_2S_4,2C_5H_5N$, NH_2Ph (+2NH_2Ph) and *benzidine* salt (+$C_{12}H_{12}N$), and *compounds* with alcohols, $C_{16}H_{10}O_8Cl_2S_4Na_2$, + 4MeOH or 3EtOH, respectively, and with $COMe_2$ (+2$COMe_2$). Degree of dispersion shows (**IV**) (high dispersion) > (**II**) > (**I**) or (**III**). Chromatographic separations are given. Adsorption of the Indigosols on cotton with or without Na_2SO_4 (increases adsorption) at 0°, 20°, 40°, 60°, and 100° are examined. Temp. of max. adsorption using Na_2SO_4 (20% on wt. of cotton) is for (**I**) ("cold-dyeing"), 0° (19·5% adsorption); (**II**), 25° (49·5%), (**III**), ~20° (6%), and (**IV**), 62° (~40%), respectively. Na_2SO_4(60%) gives greater adsorption; *e.g.*, (**II**) affords 63·5% at 25° for 1 hr. Influence of reagents on adsorption of (**II**) at 25° is examined. Thus, $MgSO_4$ acts similarly to Na_2SO_4; 10% of EtOH inhibits adsorption to some extent; H_2SO_4 (5—10% on wt. of cotton) increases adsorption to 58·5 or 43% in presence or absence of Na_2SO_4, respectively; NaOH (1—10%) decreases adsorption to 25% in presence of Na_2SO_4, whilst in absence of Na_2SO_4, NaOH (1%) decreases, and a higher conc. increases slightly, the adsorption. A. T. P.

Substance, $C_{38}H_{46}O_9N_6$, from squills glucoside and theophylline.—See A., 1941, III, 216.

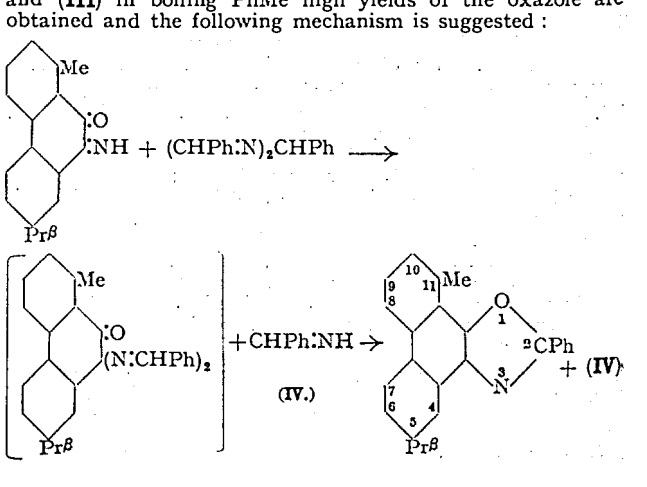
Chlorophyll. II. Separation of chlorophyll-*a* and -*b* by the chromatographic method with carbamide as adsorbent. S. Masood, A. W. Siddiqi, and M. Qureshi (*J. Osmania Univ.*, 1939, **7**, 1—4; cf. *ibid.*, 1938, **6**, 1).—In the chromatographic separation of chlorophyll-*a* and -*b* a better differentiation of zones is obtained with a 4 : 1 $CO(NH_2)_2$–talc mixture than with sugar + talc as adsorbent. F. L. U.

[Action of] esters of [α-]hydroxy-acids on [substituted] carbamides. H. Aspelund (*Finska Kem. Medd.*, 1940, **49**, 42—48).—OH·CHR·CO_2Et (R = Ph, Et) (**I**) and NHR′·CO·NHR″ (**II**) (R′ = Ph, Me; R″ = H, Ac, Me; but not all the combinations were studied) give (EtOH–NaOEt) no hydroxyacylcarbamides (*A*). (**I**) and (**II**) (R′ = Ph, R″ = H; R′ = Me, R″ = Ac) give 2 : 4-diketo-5-phenyl- or -5-ethyl-tetrahydro-oxazole probably formed by elimination of NH_2R′ (isolated as OH·CHR·CO·NHR′) from the intermediate (*A*). (**I**) and NHPh·CO·NHMe react slowly giving OH·CHR·CO·NHPh and OH·CHR·CO·NHMe with much tar; a mechanism is suggested. M. H. M. A.

Action of α-halogenated fatty acid chlorides and esters on [substituted] carbamides. H. Aspelund (*Finska Kem. Medd.*, 1940, **49**, 49—63).—CHPhCl·COCl (**I**) and NHMe·CO·NHPh (**II**) in C_6H_6 give readily *2-anilo-4-keto-5-phenyltetrahydro-oxazole* (**III**), m.p. 91°, and 1 : 5-diphenyl-3-methylhydantoin. (**III**) and dil. H_2SO_4 or HCl or (**I**) and (**II**) in dil. solution or without solvent give 2 : 4-*diketo-5-phenyltetrahydro-oxazole*, m.p. 113°, which with NaOH gives *mandelic acid methylurethane*, m.p. 127—128° (decomp.), and OH·CHPh·CO·NHMe. $CH_2Cl·COCl$ and (**II**) give *N-chloroacetyl-N′-phenyl-N-methylcarbamide*, m.p. 152°; *N-chloroacetyl-N′-methyl-*, m.p. 200—201°, and *N-phenylchloroacetyl-N′-methyl-carbamide*, m.p. 166—167°, are similarly prepared. CHPhCl·CO_2Et reacts with substituted carbamides only in presence of NaOEt, giving, *e.g.*, with NHPh·CO·NH_2 (**IV**), mainly 1 : 5-diphenylhydantoin and some (**III**) with excess of NaOEt, the proportions being reversed with a deficiency of NaOEt. $CO(NH_2)_2$ and NHAc·CO·NHMe give mainly oxazolidines in all cases, but (**II**) gives only 1 : 5-diphenyl-3-methylhydantoin with excess of NaOEt. $CH_2Cl·CO_2Et$ with (**IV**) gives mainly the hydantoin and some *2-anilo-4-ketotetrahydro-oxazole*, m.p. 235—236°, and with (**II**) the hydantoin only. M. H. M. A.

Heterocyclic nitrogen compounds. XLVII. Condensations with *iso*- and tere-phthalaldehyde. P. Ruggli and O. Schetty (*Helv. Chim. Acta*, 1940, **23**, 718—725).—*m*-$C_6H_4(CHO)_2$ (**I**) (1 mol.), NHBz·CH_2·CO_2H (2 mols.), and NaOAc (2 mols.) in Ac_2O at 100° (bath) give iso*phthalylidene-4′ : 4″-di-(2-phenyl-5-oxazolone)*, m.p. 247°, hydrolysis (aq. NaOH) of which affords BzOH but no *m*-$C_6H_4(CH_2·CO·CO_2H)_2$. *Terephthalylidene*,- m.p. 271°, and 4 : 6-*dinitro*iso*phthalylidene*-, m.p. 266°, *-4′ : 4″-di-(2-phenyl-5-oxazolone)* are similarly prepared. *iso* Phthalylidenedirhodanine (Andreasch, A., 1917, i, 663) is hydrolysed (aq. NaOH) to an amorphous product, decomp. 85°, which with conc. aq. NH_3 at 100° (bath) gives (probably) the *acid*, *m*-$CO_2H·CS·CH_2·C_6H_4·CH_2·CO·CO_2H$. iso*Phthalylidene-4′ : 4″-di-(1-phenyl-3-methyl-5-pyrazolone)*, m.p. 220°, is obtained from (**I**), 1-phenyl-3-methyl-5-pyrazolone, and a little piperidine at 110—120°. 2-Methylquinoline and 2 : 1 : 4-$NO_2·C_6H_3(CHO)_2$ with a little $CH_2Ph·NH_2$ (**II**) in EtOH afford *nitro-p-phenylenedi-(α-hydroxy-β-2-quinolylethane)*, $C_6H_4N·CH_2·CH(OH)·C_6H_3(NO_2)·CH(OH)·CH_2·C_9H_6N$, m.p. 172°. $MeNO_2$ (3 mols.), (**I**) (1 mol.), and (**II**) (0·08 mol.) at 100° (bath) yield *m-di-β-nitrovinylbenzene*, m.p. 203° (could not be nitrated; with NH_2Ph gives *m-di-β-nitro-α-anilinoethylbenzene*, m.p. 127°), the *tetrabromide*, m.p. 147°, of which with EtOH–KOAc affords *m-di-β-bromo-β-nitrovinylbenzene*, m.p. 153°. Successive treatment of this with MeOH–KOH at 100° (internal temp.) and AcOH–conc. HCl gives *m-di-(nitroacetyl)benzene*, m.p. 160°, reduced (8 H, Raney Ni) to a dark red, amorphous product. *m*-$C_6H_4Ac_2$ is not formed from (**I**) and an excess of CH_2N_2 in Et_2O; *m-phenylenedi-(ethylene oxide)*, b.p. 154°/12 mm., is obtained in an impure condition. H. B.

Preparation of derivatives of retenoxazole and reteniminazole and a study of the reaction mechanism. S. I. Kreps and A. R. Day (*J. Org. Chem.*, 1941, **6**, 140—156).—Retenquinoneimine (**I**), m.p. 108—110° (corr.), is prepared by treating retenquinone (**II**) (improved prep.) with NH_3 in EtOH. Other products are obtained when NH_3 is passed through a suspension of (**II**) in EtOH, one of which $C_{54}H_{48}O_3N_2$, m.p. 125° (corr.), appears to be of the hydrobenzamide type. In hot EtOH a mol. *complex* (1 : 1), m.p. 159—169° (corr.), of (**I**) and (**II**) results. An explanation is given of the observation that the N content of the product decreases as the time of addition of NH_3 to the EtOH solution of (**II**) is increased. (**I**) and PhCHO or *p*-OH·C_6H_4·CHO give oxazoles or iminazoles only when NH_3 is liberated either by hydrolysis of (**I**) by slight traces of H_2O present in the solvent or by alcoholysis of (**I**). (**II**), aldehyde, and NH_3 establish the necessary conditions and (**I**) is not the only intermediate essential to the reaction. With (**II**) and hydrobenzamide (**III**) in various solvents oxazole formation is observed only in those cases in which NH_3 and PhCHO are liberated, indicating that hydrolysis or alcoholysis of (**III**) precedes oxazole formation. With (**I**) and (**III**) in boiling PhMe high yields of the oxazole are obtained and the following mechanism is suggested :



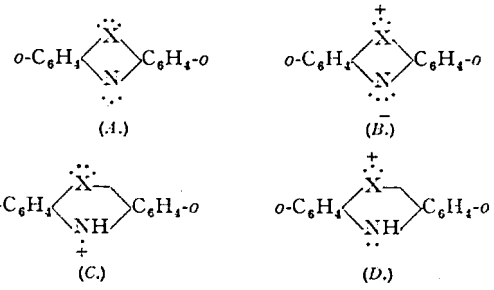
and 3(IV) → $(CHPh)_3N_2$ + NH_3. Evidence could not be adduced in favour of the view of Sircar and Sen (A., 1932, 286) that oxazole is first formed and iminazole produced therefrom by the replacement of :O by :NH. Isolation of oxazoles and iminazoles is simpler when the condensations are effected in abs. EtOH rather than in *iso*-C_5H_{11}·OH and the yields are higher in many cases. Condensations are also achieved in boiling PhMe. The best results follow the use of equiv. amounts of (II) and aldehyde in the boiling solvent and of a rapid current of dry NH_3 usually for not longer than 30 min. In cold EtOH or *iso*-C_5H_{11}·OH the yields are lower than in the hot solutions but in no case does a change of temp. alter the nature of the products. Heated PhCHO, *p*-C_6H_4Me·CHO, *o*-C_6H_4Cl·CHO, *m*-NO_2·C_6H_4·CHO, *p*-NMe_2·C_6H_4·CHO, *p*-NEt_2·C_6H_4·CHO, vanillin, anisaldehyde, veratraldehyde, piperonal, and furfuraldehyde form only oxazoles. *o*-OH·C_6H_4·CHO and *p*-OH·C_6H_4·CHO give, both hot and cold, mixtures of the corresponding oxazoles and iminazoles. The following 2-*x'*-arylretenoxazoles are described : -phenyl, m.p. 172°; -m'-*tolyl*-, m.p. 164°; -o'-*chlorophenyl*-, m.p. 155—156°; -m'-*nitrophenyl*-, m.p. 238·5°; -p'-*dimethylaminophenyl*-, m.p. 232°; -p'-*diethylaminophenyl*-, m.p. 188°, o'-*hydroxyphenyl*, m.p. 243°; -p'-*hydroxyphenyl*-, m.p. >300°; -4'-*hydroxy*-3'-*methoxyphenyl*-, m.p. 186—187°; -*anisyl*-, m.p. 172—173°; -3' : 4'-*dimethoxyphenyl*-, m.p. 204°; -3' : 4'-*methylenedioxyphenyl*-, m.p. 198·5°; -2'-*furfuryl*-, m.p. 162—163°. 2-2'- and 2-4'-*Hydroxyphenylreteniminazole* have m.p. 220—221° and >300°, respectively. M.p. are corr. H. W.

Sulphonamido-derivatives of thiazoles. J. M. Sprague and L. W. Kissinger (*J. Amer. Chem. Soc.*, 1941, **63**, 578—580).—Relative antistrepto- and antipneumo-coccal activity of the following bases are reported. New compounds are prepared by slowly adding the requisite $ArSO_2Cl$ to the aminothiazole component in C_5H_5N and then heating at 100°; N^4-acyl derivatives are hydrolysed by 2N-HCl or 10% NaOH at 100°. 2-Sulphanilamido-thiazole, m.p. 195·5—196·5°, -4-methylthiazole, m.p. 237—238° (N^4-n-*hexoyl* derivative, m.p. 171—172°), -4-phenylthiazole, forms, (by hydrolysis by HCl) m.p. 190—191° and (by hydrolysis by NaOH), m.p. 205—206° (hydrochloride, m.p. 250—254°; N^4-*Ac* derivative, m.p. 227—229°), -5-carbethoxy-4-methylthiazole, m.p. 194—196° (hydrochloride, m.p. 237—239°; N^4-*Ac* derivative, m.p. 246—248°), -5-*methyl*-4-*ethylthiazole*, m.p. 199—200° (N^4-*Ac* derivative, m.p. 230—231°), -6-*methylbenzthiazole*, m.p. 282·5—284° (N^4-*Ac* derivative, m.p. 297—299°), and -4 : 5 : 6 : 7-*tetrahydrobenzthiazole*, m.p. 249—250° (N^4-*Ac* derivative, m.p. 277—278°); 2-p-, m.p. 199·5—200°, and 2-o-*nitrobenzenesulphonamido*-4-*methylthiazole* (prepared in $COMe_2$ at room temp.), m.p. 189—190°; 2-*amino*-4 : 5 : 6 : 7-*tetrahydrobenzthiazole hydrochloride*, m.p. 249—250°; 2-*amino*-5-*methyl*-4-*ethylthiazole*, m.p. 70—71°; sulphapyridine; sulphanilamide. 2-Amino-4-methylthiazole and $PhSO_2Cl$ in aq. $NaHCO_3$, Na_2CO_3, or NaOH give 2-*dibenzenesulphon*-, m.p. 147—148°, hydrolysed by warm alkali to 2-*benzenesulphonamido*-4-*methylthiazole*, m.p. 161—162°. *p*-NHAc·C_6H_4·SO_2Cl gives similarly 2-di-N^4-acetylsulphanil-, m.p. 145—147°, and thence 2-N^4-acetylsulphanil-amido-4-methylthiazole (I). Me_2SO_4 and alkali convert (I) into 2-N^4-*acetylsulphanilmethylamido*-4-*methylthiazole*, m.p. 237—239° (giving 2-sulphanilmethylamido-4-methylthiazole, m.p. 203—204°), but *p*-NHAc·C_6H_4·SO_2Cl and 2-methylamino-4-methylthiazole (II) give an isomeric *product*, m.p. 172—173°, hydrolysed to (II) and *p*-NH_2·C_6H_4·SO_2H by acid. 2-Amino-2-thiazoline gives 80% of 2-*di*-N^4-*acetylsulphanilamido*-, m.p. 162—163°, and thence by acid or alkali 2-*sulphanilamido*-2-*thiazoline*, m.p. 204—205°. R. S. C.

Pentahydrate of 2-sulphanilamidothiazole sodium salt. H. McKennis, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 631).—This salt, +5H_2O (lost slowly in air), m.p. 55°, solidifies at 100° (loss of H_2O), remelts at 264·5° (decomp.), is prepared. R. S. C.

Sodium sulphathiazole sesquihydrate. W. G. Christiansen (*J. Amer. Chem. Soc.*, 1941, **63**, 631—632).—This *hydrate* is obtained by crystallisation from H_2O. R. S. C.

Another type of free radical in the group of thiazines and other related heterocyclic rings. L. Michaelis, S. Granick, and M. P. Schubert (*J. Amer. Chem. Soc.*, 1941, **63**, 351—355).—Electrometric titration by Br or $Pb(OAc)_4$ in 50—80% AcOH and absorption spectra indicate that phenthiazines, phenoxazines, and phenselenazines give unusually stable, half-reduced radicals, which in neutral solution exist as (*A*) (X = S, O, or Se) with a little (*B*) and in acid solution as (*C*)



(*A.*) (*B.*)

(*C.*) (*D.*)

with an approx. equal amount of (*D*). The symmetry of the resonance pair (*C*) and (*D*) and dissymmetry of the pair (*A*) and (*B*) account for the greater stability of the radicals in acid solution. The inability of $NHPh_2$ to form such resonance pairs accounts for its different behaviour. Phenthiazonium perbromide with C_5H_5N in MeOH or nicotinamide in MeOH–Et_2O gives 3 : 6-*di-pyridinium*-, +2H_2O, m.p. >298°, and -3'-*carboxylamidopyridinium-phenthiazine dibromide*, respectively. 3 : 6-*Dipyridiniumselenazine dibromide*, + 2H_2O, is similarly prepared. R. S. C.

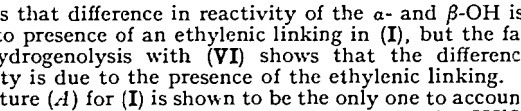
Oxidation of phenthiazine. F. DeEds (*Proc. Soc. Exp. Biol. Med.*, 1940, **45**, 632—634).—By grinding up with bentonite, phenthiazine is readily oxidised to a coloured product, probably thionol, with phenthiazone as an intermediate. V. J. W.

Photographic sensitising dyes.—See B., 1941, II, 110.

Thiamin and thiol compounds. E. S. G. Barron (*Bol. Soc. Quim. Peru*, 1940, **6**, No. 4, 7—32).—A lecture reviewing matter previously abstracted. F. R. G.

Synthesis of arecoline. P. S. Ugriumov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 48—52).—Acetonedicarboxylic acid (from citric acid) condensed with NH_2Me and MeCHO gives Me 1 : 2 : 6-trimethyl-4-piperidone-3 : 5-dicarboxylate, which with NH_2Me and CH_2O gives Me 9-keto-3 : 6 : 7 : 8-tetramethylbispidin-1 : 5-dicarboxylate (A., 1935, 629). Hot HCl converts the latter into Me 1-methyl-4-piperidone-3-carboxylate, converted by H_2–Ni–H_2O–EtOH into Me 4-hydroxy-1-methylpiperidine-3-carboxylate, which HCl–AcOH converted into arecaidine. F. R. G.

Structure of monocrotaline. VI. Structure of retronecine, platynecine, and retronecanol. R. Adams and E. F. Rogers (*J. Amer. Chem. Soc.*, 1941, **63**, 537—541; cf. A., 1941, II, 110).—The OH of retronecine (I) and similar bases, which are stable and labile to hydrogenolysis, are designated α and β, respectively. Replacement of the OH of (I) or heliotridine by Cl gives a dichloride, which with H_2–Pt gives a saturated monochloride; the Cl lost corresponds with the labile β-OH. With 1 mol. of H_2 at 2—3 atm. in presence of PtO_2 in N-HCl or of Raney Ni in EtOH, monocrotaline gives *deoxyretronecine* (III), $C_8H_{13}ON$, m.p. 77—78° (*hydrochloride*, m.p. 182—183°, $[\alpha]_D^{24}$ −15·9° in H_2O; *picrate*, m.p. 157—158°), further reduced (PtO_2; HCl) to retronecanol (IV). Hydrogenation of (I) in presence of Raney Ni at 2—3 atm. in EtOH gives slowly platynecine (V), m.p. 148—149° (corr.), $[\alpha]_D^{30}$ −57·7° in $CHCl_3$ [methiodide, m.p. 207—207·5°; Bz derivative (VI), m.p. 118—119°]. With H_2–PtO_2 in EtOH benzoylretronecine hydrochloride gives (IV) and BzOH. Formation of mono- and di-esters of (V) shows that difference in reactivity of the α- and β-OH is not due to presence of an ethylenic linking in (I), but the failure of hydrogenolysis with (VI) shows that the difference in lability is due to the presence of the ethylenic linking. The structure (*A*) for (I) is shown to be the only one to account for reactions of this series of compounds. In (V) the CH:CH is



(*A.*)

reduced to CH_2·CH_2; in (III) the β-OH is replaced by H; in (IV) both the replacement and reduction have occurred; in anhydroplatynecine the two OH are replaced by an epoxy-O; in monocrotaline the β-OH is esterified with monocrotalic acid. Difficulty in dehydrating (IV) to heliotridine is due to the fused ring system. M.p. are corr. R. S. C.

Synthesis of rutaecarpine. T. Ohta (*J. Pharm. Soc. Japan*, 1940, **60**, 109).—3-Keto-3 : 4 : 5 : 6-tetrahydro-4-carboline with isatoic anhydride (195°; 20 min.) gives rutæcarpine in good yield. H. W.

Erythrophleum **alkaloids. III. Cassaidine, a second crystalline alkaloid from the bark of** *Erythrophleum guineense* **(G. Don.) and its relation to cassaine.** L. Ruzicka and C. Dalma (*Helv. Chim. Acta*, 1940, **23**, 753—764).—The mother-liquors from the prep. of cassaine H sulphate (A., 1940, II, 28) contain *cassaidine* (**I**), $C_{24}H_{41}O_4N$, m.p. 139·5°, $[\alpha]_D^{20}$ −98±1° in 95% EtOH [*hydrochloride*, m.p. 251° (high vac.)], also isolated as the *H sulphate* (**II**), m.p. 228° (high vac.), which can be titrated using iodoeosin, Me-red, or bromophenol-blue as indicator and gives non-cryst. Ac and Bz derivatives; (**I**) contains 2 OH (Zerevitinov) but no CO. Boiling 2N-HCl hydrolyses (**II**) to $NMe_2{\cdot}[CH_2]_2{\cdot}OH$ (*aurichloride*, m.p. 194°), and *cassaidic acid* (**III**), $C_{20}H_{32}O_4$, decomp. 275—277° (high vac.; previous sintering), $[\alpha]_D^{20}$ −100±1° in 95% EtOH (Me_1 ester, m.p. 162—163°; *diacetate*, amorphous, m.p. ~90—125°), which is oxidised (CrO_3, AcOH, 35—40°) to diketo-cassenic (= dehydrocassaic) acid (*loc. cit.*). Reduction (H_2 PtO_2, AcOH) of (**I**) gives a mixture of bases from which *dihydrocassaidine*, m.p. 96—97°, $[\alpha]_D^{20}$ ±0±1° in 95% EtOH [*hydrochloride*, m.p. 247° (high vac.)], hydrolysed (aq. EtOH–KOH) to dihydroxycassanic acid (*loc. cit.*), is isolable. The absorption spectrum of (**I**) indicates that it is an αβ-unsaturated ester, viz., *β-dimethylaminoethyl cassaidate*. Cassaic acid (**IV**) (*loc. cit.*) contains CO in place of one of the CH·OH of (**III**). The possible connexion between (**III**), (**IV**), and erythrophleic acid (Blount *et al.*, A., 1940, II, 198) is discussed. M.p. are corr. Norcassaidine (A., 1936, 350) is identical with (**I**); the name should be deleted from the literature. H. B.

Modified cinchona alkaloids. VIII. Niquine. W. Solomon (*J.C.S.*, 1941, 77—83).—Niquine (**I**), niquidine, and "δ-cinchonine," transformation products of quinine, quinidine, and cinchonine respectively, form a distinct class of analogously constituted, modified cinchona alkaloids; the first two are now shown to be stereoisomerides. Quinine and HI, followed by "de-iodination" with KOH, give (**I**) [*dihydrobromide*, decomp. 242—244°, $[\alpha]_D^{15}$ −161·7° in H_2O; *acid dianisoyl-d-tartrate* (+2H_2O), decomp. 100—150°, $[\alpha]_D^{15}$ −153·0° in EtOH]. With $COMe_2$, (**I**) affords *isopropylideneniquine*, m.p. 158—160°, $[\alpha]_D^{16}$ −123·3° in EtOH, which does not react with MgMeI, thus affording additional evidence in favour of the presence of OH and NH in (**I**). Hydrogenation (PtO_2) of (**I**) yields *dihydroniquine* (**II**) (+1·5H_2O), m.p. 85°, $[\alpha]_D^{16}$ −210·1° in 0·1N-H_2SO_4 [*hydrochloride* (+H_2O), m.p. 185°, $[\alpha]_D$ −190—192° in 0·1N-HCl; *sulphate* (B_3,2H_2SO_4), m.p. 172° (decomp.); *NO*-derivative, m.p. 131°]. Methylation (Me_2SO_4–Na_2CO_3) of (**II**) gives *N-methyldihydroniquine* (+H_2O), m.p. 121°, $[\alpha]_D^{15}$ −169·9° in EtOH [*tartrate* (+1·5H_2O), m.p. 134—136°, $[\alpha]_D^{17}$ −113·1° in H_2O], and oxidation (H_2O_2) affords quininic acid and β-propylglutaric acid. Boiling of (**II**) with AcOH–H_2O yields a mixture from which *epi*-C_9-dihydroniquidine (identical with that obtained from dihydroniquidine) and dihydroniquidine [*hydrochloride* (+1·5H_2O), m.p. 238°, $[\alpha]_D^{22}$ +206·3° in 0·1N-HCl] have been obtained. (**I**) and one of the niquidines must be stereoisomerides. F. R. S.

VI.—ORGANO-METALLIC COMPOUNDS.

tert.-**Arsines and arsine oxides. II.** F. F. Blicke and S. R. Safir (*J. Amer. Chem. Soc.*, 1941, **63**, 575—576).—*p*-$C_6H_4Br{\cdot}AsO_3H_2$ with SO_2 and a trace of HI in HBr (*d* 1·55) gives p-*bromophenyldibromoarsine* (86%), b.p. 180—185°/12 mm., converted by MgMeI in Et_2O into *p*-$C_6H_4Br{\cdot}AsMe_2$, b.p. 120—125°/11 mm. (lit. 134—136°/9 mm.), and by *p*-$C_6H_4Br{\cdot}MgBr$ in Et_2O into *tri*-p-*bromophenylarsine*, m.p. 132—134°, b.p. 285—290°/7 mm., the *oxide* (prep. by $KMnO_4$ in $COMe_2$), m.p. 190—193°, of which with HNO_3 (*d* 1·6) in H_2SO_4 gives *tri*-4-*bromo*-3-*nitrophenylarsine oxide*, m.p. 252—254° (decomp.), and thence (HPO_2) *tri*-4-*bromo*-3-*nitrophenylarsine*, m.p. 189—191° (decomp.). *Di*-3-*nitro*-4-*hydroxyphenyliodoarsine*, m.p. 126—128°, is obtained from the corresponding chloroarsine by NaI in $COMe_2$.

p-$C_6H_4Br{\cdot}AsMeI$ and *p*-$C_6H_4Br{\cdot}MgBr$ in Et_2O give (*di*-p-*bromophenyl*)*methylarsine*, m.p. 71—73°, b.p. 230—240°/14 mm., oxidised by $KMnO_4$ in $COMe_2$ to the *oxide*, m.p. 221—223°, which with HNO_3 (*d* 1·6) in H_2SO_4 gives (*di*-4-*bromo*-3-*nitrophenyl*)*methylarsine oxide*, m.p. 213—215° (decomp.), converted by HPO_2 and a little HI in AcOH into (*di*-4-*bromo*-3-*nitrophenyl*)*methylarsine*, m.p. 82—84°, and by boiling aq. KOH into (*di*-3-*nitro*-4-*hydroxyphenyl*)*methylarsine oxide*, m.p. 239—240° (decomp.). R. S. C.

VII.—PROTEINS.

Solubility and titration of hæmin and ferrihæmic acid.—See A., 1941, I, 165.

VIII.—ANALYSIS.

Systematic qualitative organic micro-analysis. Comparative study of procedures of micro-extraction. W. G. Butt and H. K. Alber (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 127—132).—A detailed description is given of the construction and operation of various types of micro-extractors, and tests on these are described using salicylic acid–sand (extracted with Et_2O and EtOH), caffeine–$BaSO_4$ (EtOH), and NaCl–sand (H_2O). Tests are also described using 100 : 1, 50 : 1, 10 : 1, 1 : 10, 1 : 50, and 1 : 100 ratios of active to inert material, and a direct comparison is made of macro- and micro-Soxhlet extractors. Results are as follows. Titus and Meloche apparatus: satisfactory with 50% or more sol. material, and with high-boiling solvents. Gorbach apparatus: satisfactory with 50% or more sol. material when this is not too fine; rapid extraction, but not suitable for liquids with high surface tension. Colegrave apparatus (improved form described): satisfactory for 50% or more sol. material and for use with H_2O. Wasitzky apparatus: similar to Colegrave's. Hetterich apparatus: satisfactory for >50% sol. material and for low-boiling solvents but not satisfactory for H_2O. Many special procedures and improved types of apparatus are described, including evaporation of solvent after extraction and a new hinged circular heater. The Slotta micro-extractor is described for the first time. J. D. R.

Determination of bromine addition number. K. Uhrig and H. Levin (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 90—92).—The sample in $CHCl_3$ is titrated with standard Br in AcOH until a yellow colour persists. With dark substances, an external starch indicator is used. J. D. R.

Determination of the acetyl group. J. R. Matarett and J. Levine (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 98—99).—The substance with EtOH and HCl is distilled in a special apparatus (consisting of distillation flask with long column and take-off at the head of the column) and the distillate of EtOAc is collected in 0·1N-NaOH and determined by sap. val. *N*-Ac requires more HCl and a longer distillation than *O*-Ac, but accuracy in both cases is good. J. D. R.

Determination of amino-acids by the ninhydrin reaction. B. E. Christensen, E. D. West, and K. P. Dimick (*J. Biol. Chem.*, 1941, **137**, 735—738).—The determination of NH_2-acids by the ninhydrin reaction (Mason, A., 1938, II, 252) in the apparatus of West *et al.* (A., 1940, III, 369) is described. Results agree with Kjeldahl determinations to within 1%. A. Li.

Colour reaction of aromatic nitro-compounds. S. Nisida (*Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 20—24).—NO_2-compounds (2—3 mg.) in $COMe_2$ (2—3 c.c.) often give coloured solutions when treated with 2N-KOH or -NaOH (2 drops). $(NO_2)_1$-compounds give colourless or pale yellow solutions. 2 : 4-$(NO_2)_2$-compounds give blue solutions if position I is occupied by Me and red colours with other groups at 1. $(NO_2)_2$- and $(NO_2)_3$-compounds with other arrangements of the NO_2-groups give colourless or faintly coloured solutions. J. L. D.

Reduction–oxidation method for determination of vitamin-K_1 and associated quinones and naphthaquinones. N. R. Trenner and F. A. Bacher (*J. Biol. Chem.*, 1941, **137**, 745—755).—Vitamin-K_1 and related quinones are determined in 95% EtOH or Bu^{n}OH by reduction (H_2, Raney Ni in presence of phenosafranine) and subsequent titration with 2 : 6-dichlorophenol-indophenol. Titration vals. depend on the oxidation–reduction potential of the substance being titrated, hence samples are compared with a standard. Vegetable and cod-liver oils cause no interference. A. Li.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JUNE, 1941.

I.—ALIPHATIC.

Direct determination of oxygen in organic compounds by hydrogenation. II. Cracking mechanism on platinum–silica gel catalyst. K. Morikawa, T. Kimoto, and R. Abe (*Bull. Chem. Soc. Japan*, 1941, **16**, 33—39).—The production of H_2O, CO_2, and CO by passing H_2 and the vapours of sucrose, $H_2C_2O_4$, BzOH, anthraquinone, and $Na_2C_2O_4$ over Pt–SiO_2 gel, varying the temp. (800—950°) and rate of H_2 flow, has been studied. High temp. gives a high proportion of CO. The vapours from H_2O or $NaHCO_3$ when passed with H_2 over Pt–SiO_2 gel containing free C give 95% of CO. It is concluded that in the cracking process the following reactions occur: $C + CO_2 = 2CO$; $C + H_2O = CO + H_2$; $CO_2 + H_2 = CO + H_2O$. A. Li.

Separation of pure methane from other gaseous hydrocarbons by selective adsorption.—See B., 1941, II, 69.

Preparation of ββ- and γγ-dimethylpentane. H. Soroos and H. B. Willis (*J. Amer. Chem. Soc.*, 1941, **63**, 881).—Prep. of CH_2EtBu^{γ} from $Bu^{\gamma}Cl$–$MgPr^{\alpha}Cl$ (27%) or –$MgPr^{\alpha}Br$ (29%) and of CMe_2Et_2 from CMe_2EtCl–MgEtCl (43%) or –MeEtBr (41%) is reported (cf. Wibaut *et al.*, A., 1939, II, 237; Edgar *et al.*, A., 1929, 789). R. S. C.

Isomerising action of cyclising catalysts.—See A., 1941, I, 216.

ξ-Bromo-βζκ-trimethyl-*n*-pentadecane. P. G. Smith and C. E. Schweitzer (*J. Amer. Chem. Soc.*, 1941, **63**, 882).—Pr^{β}·$[CH_2]_3$·CHMe·$[CH_2]_3$·CHMe·$[CH_2]_3$·COMe and Na–$Pr^{\beta}OH$ give the alcohol, b.p. 146—148°/1 mm., and thence by PBr_3 in light petroleum *ξ-bromo-βζκ-trimethyl*-n-*pentadecane*, b.p. 138—140°/1 mm. R. S. C.

Estimation of unsaturated hydrocarbons by bromine addition. S. J. Green (*J. Inst. Petroleum*, 1941, **27**, 66—71).—In the Br′–OBr′ method for brominating olefines, the amount of excess reagent is crit. since inhibition of bromination occurs when low [Br] are used. The Lewis and Bradstreet titration technique is preferred to the Francis method as it appears to avoid this inhibition effect. If Br no. is accepted as a guide to the degree of unsaturated compounds, the conditions of the reaction must be very precisely specified. The % of unsaturated compounds cannot be determined unless the mol. wts. and nature of the olefines present can be determined. T. C. G. T.

Catalytic polymerisation of normally gaseous olefines.—See B., 1941, II, 106.

Polymerisation of olefines. II. Co-polymerisation of *sec.*- and *tert.*-butyl alcohols by sulphuric acid. F. C. Whitmore, K. C. Laughlin, J. F. Matuszeski, and J. D. Surmatis (*J. Amer. Chem. Soc.*, 1941, **63**, 756—757).—Addition of $Bu^{\gamma}OH$ to *sec.*-BuOH in 75% (wt.) H_2SO_4 at 64° results in union of Bu^{γ} with *sec.*-Bu (75%) and Bu^{γ} (25%). The products, $CHBu^{\gamma}$:CHMe (I) (40%), $CMePr^{\beta}$:CHMe (35%) [formed by rearrangement of (I)], and di*iso*butylenes (25%), are identified by fractionation and subsequent ozonisation. R. S. C.

[Catalytic] polymerisation of unsaturated hydrocarbons.—See A., 1941, I, 215.

Structure of additive compounds of metallic halides and unsaturated hydrocarbons. S. L. Varschavski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 29, 315).—CH_2:CHCl is produced when CHCl:CH·HgCl (obtained by passing C_2H_2 into saturated aq. NaCl containing $HgCl_2$) is treated with 40% HBr or conc. HCl. The results support the views of Freidlina and Nesmejanov (A., 1940, II, 246). W. McC.

[Photometric] determination of small traces of solvent vapours in air.—See A., 1941, I, 178.

Formation of trichloroacetic acid from perchlorethylene by atmospheric oxidation. K. C. Bailey and W. S. E. Hickson (*J.C.S.*, 1941, 145).—Exposure of C_2Cl_4 with a trace of H_2O to sunlight for 4 months yields CCl_3·CO_2H (extracted by H_2O). A. Li.

Derivatives of allylic chlorides. Reactions of methallyl chloride involving the double linking. J. Burgin, G. Hearne, and F. Rust (*Ind. Eng. Chem.*, 1941, **33**, 385—388).—Hydration of CH_2:CMe·CH_2Cl (I) to OH·CMe_2·CH_2Cl (II) (63% yield) is effected by 80% H_2SO_4 at 5—10° for 2·5 hr. CMe_2:CHCl (III) and 90% H_2SO_4 at −10° to 0° give (II) (66% yield). Other acids, *e.g.*, 85% H_3PO_4, 70% HNO_3, $PhSO_3H$, or 60% $HClO_4$ (very effective, apart from explosion danger), can be used, but each has a sp. optimum temp. and concn. range. (I) and 80% H_2SO_4 (or H_3PO_4) at 40° give (III) (85% yield) (equilibrium reaction); the passage of the vapour over activated Al_2O_3 gives a similar result. (III), b.p. 68·1°, is purified by refluxing with 10% KOH–EtOH, which hydrolyses (I). Chlorination of (I) or (III) at room temp. affords ~70% yield of isomeric dichloro*iso*butenes, CH_2:$C(CH_2Cl)_2$ and CHCl:CMe·CH_2Cl, in approx. equal amounts. Direct chlorohydrination of (I) by dil. Cl_2–H_2O at 30° (apparatus is described) (Cl_2 bubbled into aq. solution gives a poor result) affords ~70% of OH·$CMe(CH_2Cl)_2$, b.p. 69°, with small amounts of trichloro*tert.*-butyl alcohols, unsaturated dichlorides, tetrachloro*iso*butanes, and $CMeCl(CH_2Cl)_2$. Mechanisms of reactions are given. CH_2:CMe_2 is more reactive to HCl or Cl_2 than is (I); for hydration, 65% H_2SO_4 is the max. concn. possible to avoid excessive polymerisation. A. T. P.

Nitration of hydrocarbons.—See B., 1941, II, 106.

Preparation of unsaturated higher alcohols. VII. S. Komori (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 428—430B).—A series of Cr_2O_3–Fe_2O_3 catalysts are shown to accelerate the hydrogenation of the Et ester of rice oil or erucic acid to docosenol at ~313—340°/80—100 atm. Fe_2O_3 alone is less satisfactory but utilisable if its proportion is high. H. W.

Catalytic dehydrogenation and condensation of aliphatic alcohols. V. I. Komarewsky and J. R. Coley (*J. Amer. Chem. Soc.*, 1941, **63**, 700—702).—In presence of Cr_2O_3 at 400—425°, *n*-hexyl, -heptyl, and -octyl alcohol give the ketone according to the equation, $2CH_2R·OH \rightarrow COR_2 + CO + 3H_2$, but at 475—525° less ketone and ~2·5% of phenol [PhOH, *o*-cresol, and *m*-2-xylenol (by rearrangement of *o*-C_6H_4Et·OH), respectively] are obtained. Cr_2O_3–Al_2O_3 (A., 1939, II, 49) is thus a true " complex action " catalyst. R. S. C.

Synthetic glycerin [and allyl alcohol] from petroleum [propylene].—See B., 1941, II, 69.

Preparation of pentaerythritol.—See B., 1941, II, 106.

Halogenation in reactive solvents. VII. Chlorination of olefines in reactive solvents with *tert.*-butyl hypochlorite. C. F. Irwin and G. F. Hennion (*J. Amer. Chem. Soc.*, 1941, **63**, 858—860; cf. A., 1940, II, 295).—(*a*) *cyclo*Hexene, (*b*) CH_2:$CHBu^{\alpha}$, and (*c*) $(CHEt{:})_2$ with Cl_2 in MeOH give (*a*) 17·6 and 82·3, (*b*) 31·6 and 68·3, and (*c*) 34·7 and 65·2% of dichloride and chloro-ether, CHRCl·CHR′·OMe, respectively, the proportions being determined from the Cl-content of the product. Olefines and ROH [R = *n*-alkyl, OAc, or (in C_6H_5) Ph] in presence of $Bu^{\gamma}OCl$ (and, if R = alkyl, a little *p*-$C_6H_4Me·SO_3H$ as catalyst) at a suitable controlled temp. (5—60°) give only (35·5—77·7%) the chloro-ether. Thus are obtained $CH_2Cl·CHMe·OMe$, b.p. 100—101°/743 mm., *β-chloro-γ-methoxy-γ-methylbutane*, b.p. 134—135°/749 mm., *β-chloro-γ-methoxy*-n-*pentane*, b.p. 75—77°/100 mm., 1-*chloro*-2-*methoxy*cyclo*hexane*, b.p. 73—74°/20 mm., *γ-chloro-δ-*

methoxy-n-*hexane*, b.p. 94—95°/98 mm., *β-chloro-γ-ethoxy*-n-*pentane*, b.p. 69—70°/50 mm., *β*-methoxy-, b.p. 123°/100 mm., *-ethoxy-*, b.p. 98°/28 mm., -n-*propoxy-*, b.p. 104—105°/20 mm., and -n-*butoxy*-n-*heptyl chloride*, b.p. 128—129°/30 mm., $(Cl\cdot[CH_2]_2)_2O$, $Cl\cdot[CH_2]_2\cdot OAc$, *β-chloroisopropyl acetate*, b.p. 147—149°/745 mm., *γ-chloro-β-acetoxy-β-methylbutane* (22·4%), b.p. 99—101°/100 mm. (with 47·5% of $CMeCl{:}CMe_2$, b.p. 91—92°/741 mm.), *β-chloro-γ-acetoxy*-n-*pentane*, b.p. 73—75°/20 mm., *γ-chloro-δ-acetoxy*-n-*hexane*, b.p. 124—126°/100 mm., *α-chloro-β-acetoxy*-n-*heptane*, b.p. 119—120°/20 mm., *β-phenoxy*-n-*propyl chloride*, b.p. 110—113°/22 mm., and *β-phenoxy*-n-*heptyl chloride*, b.p. 138—140°/8 mm.

R. S. C.

[Kinetics of] synthesis of diethyl acetal.—See A., 1941, I, 171.

Use of Bunte salts in synthesis. I. Preparation of mercaptals. H. E. Westlake, jun., and G. Dougherty (*J. Amer. Chem. Soc.*, 1941, **63**, 658—659).—RHal and $Na_2S_2O_3$ in boiling 50% EtOH give $SR\cdot SO_3Na$ (not isolated), which, after removal of the EtOH, with R'CHO in boiling aq. HCl give 46—77% of $CH_2(S\cdot CH_2Ph)_2$, $CHPh(S\cdot CH_2Ph)_2$, $CH_2(SBu)_2$, $CHMe(SBu)_2$, $CH_2(SEt)_2$, and *formaldehyde di-(β-hydroxyethyl) mercaptal*, b.p. 52—54°/5 mm. R. S. C.

Anhydrides of normal aliphatic saturated monobasic acids. J. M. Wallace, jun., and J. E. Copenhaver (*J. Amer. Chem. Soc.*, 1941, **63**, 699—700).—The following are prepared by boiling RCO_2H in $AcOH–Ac_2O$: heptoic, m.p. −10·8°, octoic, m.p. 0·9±0·1°, nonoic, m.p. 14·8°, decoic, m.p. 24·7±0·2°, undecoic, m.p. 36·7°, lauric, m.p. 42·1±0·1°, *tridecoic*, m.p. 49·9±0·2°, myristic, m.p. 53·5±0·1°, *pentadecoic*, m.p. 60·6°, palmitic, m.p. 63·9°±0·1°, *margaric*, m.p. 67·6°, and stearic, m.p. 70·7°, anhydride. There is little evidence of alternation in m.p. above C_5. R. S. C.

Methacrylic resins. I. Polymerisation of methyl methacrylate. R. Inoue (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 448—449B).—$CH_2{:}CMe\cdot CO_2Me$ (purification described) is sealed into hard glass tubes, which are then placed in a thermostat for polymerisation in the absence of light. The amount of polymeride (I) is determined by dissolving the weighed sample in $COMe_2$ or C_6H_6 and pptg. (I) by MeOH. (I) is then dried at ~80° for a week and then weighed. The rate of polymerisation accelerates with time to a max., after which it decreases continuously. From the val. dx/dT at 10% yield of (I) and polymerisation temp. T° K. the apparent heat of activation is ~12·5 kg.-cal. The degree of polymerisation of (I) formed at various stages during a polymerisation is almost the same; it increases with decreasing temp. o polymerisation. H. W.

Direct esterification of higher fatty acids with glycerol. V. Esterification of two-component fatty acid mixture into monoglyceride. S. Kawai (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 428B).—Complete esterification occurs when equimol. mixtures of stearic (I) and oleic acid (II), (I) and lauric acid (III), and (II) and (III) are heated for ~60 min. at 220—250° with glycerol (1·4 mols. per mol. of acid). The products contain considerable amounts of di- and tri- in addition to mono-glycerides. In the esterification of (I) + (II) and (I) + (III) the formation of mono-olein (IV) or monolaurin (V) predominates over that of monostearin whilst with (II) + (III) the production of (V) appears readier than that of (IV). H. W.

Ester interchange between oils and glycerol. III. Experiments on sperm-head oil and kurokozame oil. S. Kawai (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 427B).—Addition of Zn and oleic acid accelerates the interchange resulting in the rapid formation of the oils of higher OH vals.; judging from these vals. ester interchange occurs in the glyceride structure and in the wax ester compositions and therefore produces a considerable amount of free higher alcohols (*A*). The portion of the product insol. in EtOH appears to consist mainly of triglycerides and unchanged esters whilst the sol. portions (*B*) contain predominatingly mono- (and also di-)glycerides and *A* and *B* are suitable materials for the manufacture of sulphonated oil etc. H. W.

Isomeric structure of the C_{18} unsaturated [fatty] acids from their Raman and infra-red spectra. J. W. McCutcheon, M. F. Crawford, and H. L. Welsh (*Oil and Soap*, 1941, **18**, 9—11).—A study of the Raman and infra-red spectra of highly purified specimens of the Et esters of the respective acids has led to the conclusion that all the double linkings of the naturally occurring oleic, linoleic (as also of *β*-linoleic acid), and linolenic acids have the *cis*-configuration, whilst the esters of elaidic and linelaidic acid (prepared by the method of Kass and Burr, A., 1939, II, 297) contain only *trans*-linkings. An alternative explanation, consistent with the above conclusions, is suggested for the experimental results obtained by Bertram and Kipperman (B., 1935, 1149), which were interpreted by them as indicating a *trans*-structure of oleic acid. E. L.

Influence of solvents on auto-oxidation of methyl linoleate. T. R. Bolam and W. S. Sim (*J.S.C.I.*, 1941, **60**, 50—56).—In the auto-oxidation of Me linoleate at 75° in absence of solvent, or in solution in AcOH or a hydrocarbon solvent, a peroxide group is formed at one double linking and a ketol at the other. The peroxide undergoes change, probably as the result of polymerisation, and the ketol group is enolised to an extent depending on the conditions. In AcOH the initial rate of oxidation and the rate of change of peroxide are ≫ in hydrocarbons or in absence of solvent, the hydrocarbons acting simply as diluents. With chloroacctic acids, the initial rate of absorption is still further increased, the effect being the more marked the greater is the degree of substitution. The rate of absorption is not increased in alcoholic solution, so that factors other than the polar or non-polar nature of the solvent are involved. Since the max. rate of absorption occurs at an earlier stage in AcOH than in hydrocarbons, the rate of oxidation is probably determined by the concn. of free peroxide. Volatile oxidation products are formed to a very limited extent.

Catalysis by ascorbic acid.—See A., 1941, I, 215.

Manufacture of lævulic acid.—See B., 1941, II, 107.

Catalytic oxidation of benzene [to maleic acid].—See B., 1941, II, 107.

Oxidation processes in platinum oxalates.—See A., 1941, I, 217.

Condensation of bromoacetaldehyde with malonic acid. N. S. Vulfson and M. M. Schemjakin (*Compt. rend. Acad. Sci., U.R.S.S.*, 1940, **29**, 206—207).—Condensation of $CH_2Br\cdot CHO$ (I) with $CH_2(CO_2H)_2$ (II) in presence of piperidine at room temp. and subsequently at 105—115° gives a small amount of the *β-lactone*, $CH_2Br\cdot CH<\overset{O}{\underset{CH(CO_2H)}{\frown}}>CO$ (*Ag* salt), hydrolysed by alkali to (I) and (II). H. W.

Mechanism of the primary photodissociation of organic molecules.—See A., 1941, I, 173.

Production of formaldehyde in a high- and low-frequency arc.—See A., 1941, I, 172.

Catalysis by activated copper sulphide.—See A., 1941, I, 215.

Production of acraldehyde.—See B., 1941, II, 73.

Formation of polyhydroxydialdehydes. I. Xylotrihydroxyglutardialdehyde and its derivatives. K. Iwadare (*Bull. Chem. Soc. Japan*, 1941, **16**, 40—44).—Oxidation $[Pb(OAc)_4$ in $C_6H_6]$ of 1 : 2-*iso*propylidene-*d*-glucofuranose yields 1 : 2-iso*propylidene*-d-*xylotrihydroxyglutardialdehyde* (I), b.p. 132—136°/0·01—0·02 mm., $[\alpha]_D^{16}$ +20°±3° in EtOH [*monophenylhydrazone*, m.p. 140·5—141° (corr.), $[\alpha]_D^{19}$ −41°±1° in $CHCl_3$; *monosemicarbazone*, m.p. 209—209·5° (corr.; decomp.)], hydrolysed (0·1N-H_2SO_4) to *xylotrihydroxyglutardialdehyde* (II) [*bisphenylhydrazone*, m.p. 126·5—127·5° (corr.); *bis*-p-*nitrophenylhydrazone*, m.p. 191—192° (corr.; decomp.). (I) and (II) with $SrCO_3$ and aq. Br yield *Sr* 1 : 2-iso*propylidene*-d-*xyluronate* and d-*xyluronate*, respectively. A. Li.

Synthesis of acetone from acetylene.—See B., 1941, II, 105.

Action of fluorine on organic compounds. X. Vapour-phase fluorination of acetone. N. Fukuhara and L. A. Bigelow (*J. Amer. Chem. Soc.*, 1941, **63**, 788—791).—Apparatus for vapour-phase fluorination of volatile org. compounds is described. $COMe_2$ and F_2–N_2 at ≮60° give exothermally COF_2, CF_4, mono-, b.p. 78° (lit. 72·5°) [semicarbazone, m.p. 132° (decomp.)], and *hexa-fluoroacetone*, m.p. −129°, b.p. −28° [*semicarbazone*, $+H_2O$ and anhyd., m.p. 153° (decomp.)], $CF_3\cdot COF$, b.p. −59° (derived amide, m.p. 74—75°), *oxalyl fluoride*, b.p. 28° [with MeOH and then liquid NH_3 gives $(CO\cdot NH_2)_2$], (?) O_2F_2, and other products. A free-radical mechanism is proposed. R. S. C.

Qualitative chemical identification of the natural sugars. W. E. Militzer (*J. Chem. Educ.*, 1941, **18**, 25—28).—Procedures for carrying out numerous well-known tests are given. The tests are arranged in a systematic scheme for identifying the sugars. L. S. T.

Industrial uses of cane sugar. I. Catalytic effects of pyridine on the acetylation of sucrose. M. Amagasa and T. Yanagita (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 444—445B).—At 130—140° C_5H_5N is a very active catalyst of the action of Ac_2O on sucrose, giving a higher yield of sucrose octa-acetate than can be obtained by use of anhyd. NaOAc. The progress of acetylation can be accurately followed by thermometric titration. H. W.

Chemistry of galactogen from *Helix pomatia*. *l*-Galactose as a component of a polysaccharide of animal origin. D. J. Bell and E. Baldwin (*J.C.S.*, 1941, 125—132; cf. A., 1941, III, 111).—Galactogen (I) hydrolysatc after removal of *d*-galactose yields by the method of Moore and Link (A., 1940, II, 244) 2-dl-*galactobenziminazole*, m.p. 233°. A fraction of the methanolysis product of methylated (I) yields 2 : 3 : 4 : 6-*tetramethyl*-dl-*galactoseanilide*, $[\alpha]_D$ −2° in $COMe_2$, m.p. (and mixed m.p. with synthetic product) 179—181°. It is concluded that (I) is composed of units having 7 galactose radicals, 3 " backbone " radicals of *d*-galactose and 4 side-chains, 3 of *d*- and one of *l*-galactose. The structure of the unit is discussed. A. Li.

Separation of trimethylamine from mixture with mono- and di-methylamine.—See B., 1941, II, 107.

Aldol condensations with aliphatic Schiff's bases. W. S. Emerson, S. M. Hess, and F. C. Uhle (*J. Amer. Chem. Soc.*, 1941, **63**, 872).—When $Pr^{\alpha}CHO$ and NH_2Bu^{α} are heated at 20 mm., N-n-*butylidene*-n-*butylamine* (85%), b.p. 140—145°, distils. When boiled, this gives 65% of γ-n-*butyliminomethyl*-Δγ-n-*heptene* (I), b.p. 217—220°, hydrolysed by boiling 6N-HCl to $CHPr^{\alpha}{:}CEt{\cdot}CHO$. Formation of (I) occurs by way of $NHBu^{\alpha}{\cdot}CHPr^{\alpha}{\cdot}CHEt{\cdot}CH{:}NBu^{\alpha}$. R. S. C.

Synthesis of *N*-trimethylglycylcholine. T. S. Work (*J.C.S.*, 1941, 190—191).—$Br{\cdot}[CH_2]_2{\cdot}O{\cdot}CO{\cdot}CH_2Br$, or (poor yield) *β-bromoethyl chloroacetate*, b.p. 112—114°/22 mm. (from $CH_2Cl{\cdot}COCl$ and $CH_2Br{\cdot}CH_2{\cdot}OH$ at >50°), with NMe_3 in a sealed tube yields the *dibromide*, m.p. 238°, of trimethylglycylcholine [*dipicrate*, m.p. 244°; aurichloride, m.p. ~250° (decomp.); *platinichloride*, m.p. indefinite]. The crude dichloride is similarly obtained from $Cl{\cdot}[CH_2]_2{\cdot}O{\cdot}CO{\cdot}CH_2Cl$. A. Li.

Reduction of fatty acid amides at high pressures. II. Reduction of anilides. S. Ueno, S. Takase, and Y. Tajima (*J. Soc. Chem. Ind. Japan*, 1941, **44**, 58—59B).—Lauric, myristic, or palmitic acid and NH_2Ph at 200° give the corresponding *anilides*, m.p. 75°, 84°, or 87°, respectively, hydrogenated at ~280°/~100—200 atm. for ~3 hr. to *di*-n-*dodecyl*-, m.p. 53°, -*myristyl*-, m.p. 56°, or -*cetyl-amine*, m.p. 64°, respectively. A. T. P.

Ethylenediamine. IV. Monoalkyl derivatives. S. R. Aspinall (*J. Amer. Chem. Soc.*, 1941, **63**, 852—854; cf. A., 1940, II, 289).—70% aq. $(CH_2{\cdot}NH_2)_2$ and EtOAc at room temp. give $NH_2{\cdot}[CH_2]_2{\cdot}NHAc$ (60%) [with a little $(CH_2{\cdot}NHAc)_2$], converted (Schotten–Baumann) into $NHAc{\cdot}[CH_2]_2{\cdot}NH{\cdot}CO_2Ph$, m.p. 103° (lit. 105°), which with RHal and KOH in boiling EtOH gives $SO_2Ph{\cdot}NR{\cdot}[CH_2]_2{\cdot}NHAc$, whence conc. HCl liberates (80% yields) $NH_2{\cdot}[CH_2]_2{\cdot}NHR$. Examples are R = Me, b.p. 115—116°/757 mm. [dipicrate, m.p. 220°; Bz_2, m.p. 112°, and $(SO_2Ph)_2$ derivative, m.p. 94°], Et, b.p. 129—131°/759 mm. [*dipicrate*, m.p. (anhyd. and + solvent) 195°; Bz_2, m.p. 120°, and $(p\text{-}C_6H_4Br{\cdot}SO_2)_2$ derivative, m.p. 126°], and CH_2Ph, b.p. 100°/4 mm. [dipicrate, m.p. 222° (decomp.); Bz_2, m.p. 188°, and $(p\text{-}C_6H_4Br{\cdot}SO_2)_2$ derivative, m.p. 198°. R. S. C.

Amino-acid constituent of ox brain kephelin.—See A., 1941, III, 343.

Glycyl-*l*-methionine. W. C. Hess and M. X. Sullivan (*J. Amer. Chem. Soc.*, 1941, **63**, 881—882).—*Chloroacetyl*-l-*methionine* (prep. by $CH_2Cl{\cdot}COCl$ in N-NaOH), m.p. 105—107°, and 25% aq. NH_3 at 70° give 57—64% of *glycyl*-l-*methionine*, m.p. 140—145°. R. S. C.

Introduction of substituted vinyl groups. VII. Alkylidene- and substituted vinyl-alkylmalononitriles. A. C. Cope and K. E. Hoyle (*J. Amer. Chem. Soc.*, 1941, **63**, 733—736; cf. A., 1940, II, 85).—With a little piperidine in C_6H_6 (exothermic reaction) or piperidine and AcOH or NH_4OAc–AcOH in boiling C_6H_6 or without other catalyst in AcOH at 100°, *cyclo*hexanone (I) and $CH_2(CN)_2$ give cyclo*hexylidenemalononitrile* (II), b.p. 137—138°/10 mm., whence O_3 in C_5H_{12} regenerates (I). With NH_4OAc–C_6H_6 or piperidine in AcOH, $CH_2(CN)_2$ and the appropriate ketone give *α-ethylpropylidene*- (III), b.p. 122—125°/23 mm., *α-methylbutylidene*- (IV), b.p. 110—113°/12 mm., and iso*propylidene-malononitrile* (V), b.p. 107—108°/23 mm. The cryst. products previously considered to be (II) and (V) are dimerides. The monomeric products polymerise when boiled or kept with piperidine [(V) so rapidly that it cannot be alkylated (see below)], and a dimeride, m.p. 168—170° (softens at 158°), of (V) is isolated. Treatment of (II), (III), or (IV) with $NaOPr^{\beta}$–$Pr^{\beta}OH$ at 50° and then with EtI, first at 0° and then at the b.p., gives *ethyl*cyclo*hexenyl*-, b.p. 153—154°/20 mm., *ethyl-α-ethylpropenyl*-, b.p. 128—130°/29 mm., and *ethyl-α-methylbutenyl-malononitrile*, b.p. 121—124°/24 mm., identified by conversion into the derived barbituric acids. The Na derivative of (IV) with EtI, EtBr, or Et_2SO_4 in $Pr^{\beta}OH$ or EtOH gives the imino-ether, $CHEt{:}CMe{\cdot}CEt(CN){\cdot}C(OEt){:}NH$, b.p. (impure) 142·5—143°/26 mm. R. S. C.

Manufacture of mono- and di-methylformamides.—See B., 1941, II, 107, 108.

Grignard reductions. IX. Reduction of acid halides. F. C. Whitmore, J. S. Whitaker, W. A. Mosher, O. N. Breivik, W. R. Wheeler, C. S. Miner, jun., L. H. Sutherland, R. B. Wagner, T. W. Clapper, C. E. Lewis, A. R. Lux, and A. H. Popkin (*J. Amer. Chem. Soc.*, 1941, **63**, 643—654).—Interaction of RCOCl with MgR'Hal proceeds by independent reactions: (*a*) → CORR' → CHRR'·OH, and (*b*) RCOCl + MgR'Hal → $MgHal_2$ + RCHO + olefine, followed by RCHO + MgR'Hal → $CH_2R{\cdot}OH$ + MgHal·OH + olefine and RCHO → CHRR'·OH. $CH_2Bu^{\gamma}{\cdot}CMeBu^{\gamma}{\cdot}COCl$ with MgBu$^{\gamma}$Cl or $CMe_2Et{\cdot}MgCl$ gives ~70% of $CH_2Bu^{\gamma}{\cdot}CMeBu^{\gamma}{\cdot}CHO$, but owing to further reaction ≯ traces of other aldehydes are obtained. Free Mg has no effect on the reaction; RCOCl and RCOBr react similarly, but RCOI gives by-products ($CHEt_2{\cdot}COHal$–MgBu$^{\gamma}$Cl). MgR'Cl, MgR'Br, and MgR'I give similar results. Essentially the same reactions occur whether RCOCl is added to MgR'Hal or vice versa, but in the latter case $CH_2R{\cdot}OH$ is obtained as ester. Lowering the temp. increases slightly the amount of ketone isolated. Et and Bu esters are formed in small amount by interaction of RCOCl with the solvent Et_2O or Bu_2O in presence of $MgCl_2$. Some RCO_2CHRR' is also formed. Increasing the concn. of MgR'Hal slightly increases the yield of $CH_2R{\cdot}OH$ (MgBu$^{\gamma}$Cl–$CHEt_2{\cdot}COCl$). Reduction to $CH_2R{\cdot}OH$ is best obtained by adding RCOCl gradually with stirring to 2—3 mols. of MgR'Hal. Branching or larger size of R or R' greatly increases the amount of reduction. RCO_2Na is not reduced by $CMe_2Et{\cdot}MgCl$ (a good reducing agent) in Et_2O. Addition of $CHEt_2{\cdot}COCl$ (134·5) to MgBu$^{\gamma}$Cl gives $CHEt_2{\cdot}CHBu^{\gamma}{\cdot}OH$ (I) (88·3), b.p. 131—132°/150 mm. (*α-naphthylurethane*, m.p. 101—102°), $CHEt_2{\cdot}CH_2{\cdot}OH$ (II) (21·7), b.p. 103°/150 mm., and C_2Me_6 (21·7 g.). $CHEt_2{\cdot}CHO$ and MgBu$^{\gamma}$Cl in Et_2O give (I) and a little (II). $CHEt_2{\cdot}COBu^{\gamma}$ [prepared from (I) by $K_2Cr_2O_7$], b.p. 120·5—121°/150 mm., and MgBu$^{\gamma}$Cl in boiling Et_2O (not at 25°) give 38% of (I). Addition of $CHEtBu^{\alpha}{\cdot}COCl$ to MgBu$^{\gamma}$Cl gives 64% of $CHEtBu^{\alpha}{\cdot}CHBu^{\gamma}{\cdot}OH$ (III), b.p. 105°/17 mm. (*phenylurethane*, m.p. 96—97°), and 29·6% of $CHEtBu^{\alpha}{\cdot}CH_2{\cdot}OH$ (IV), b.p. 133—134°/150 mm. [oxidised by CrO_3 to $CHEtBu^{\alpha}{\cdot}CO_2H$ (anilide, m.p. 88·5—89·5°)]. The acetate, b.p. 170°/150 mm., of (III) at 480—500° gives $CEtBu^{\alpha}{:}CHBu^{\gamma}$, oxidised by O_3 to Bu$^{\gamma}$CHO and $COEtBu^{\alpha}$. Addition of $CHEtBu^{\alpha}{\cdot}COCl$ to MgBu$^{\gamma}$Cl and MgI_2 gives 42·8% of (III) and 19·3% of (IV). Addition of Bu$^{\gamma}$COCl to MgBu$^{\beta}$I gives 74% of $CH_2Bu^{\gamma}{\cdot}OH$, and of $CH_2Bu^{\gamma}{\cdot}COCl$, b.p. 94°/100 mm., to MgBu$^{\gamma}$Cl gives 67% of $Bu^{\gamma}{\cdot}[CH_2]_2{\cdot}CHBu^{\gamma}{\cdot}OH$ (V), m.p. 58—59° [acetate, b.p. 152°/150 mm.; proof of structure as for (III)], and 13·5% of $Bu^{\gamma}{\cdot}[CH_2]_3{\cdot}OH$. Addition of MgBu$^{\gamma}$Cl to (*a*) $Pr^{\alpha}COCl$ or (*b*) $Pr^{\beta}COCl$ gives (*a*) 21% of $COPr^{\alpha}Bu^{\gamma}$, 11·6% of $Bu^{\alpha}CO_2Bu^{\alpha}$, and 36·8% of $Pr^{\alpha}CO_2CHPr^{\alpha}Bu^{\gamma}$, and (*b*) 45% of $Pr^{\beta}CO_2CHPr^{\beta}Bu^{\alpha}$, b.p. 131°/100 mm., 19% of $Pr^{\beta}CO_2Bu^{\beta}$, and 17·7% of $COPr^{\beta}Bu^{\gamma}$. Addition of Bu$^{\gamma}$COCl to $CH_2Bu^{\gamma}{\cdot}MgCl$ gives 87% of $Bu^{\gamma}{\cdot}[CH_2]_2{\cdot}COBu^{\gamma}$, b.p. 108—110°/150 mm. [reduced by $Al(OPr^{\beta})_3$ to (V) (cf. lit.)], and a trace of $CH_2Bu^{\gamma}{\cdot}OH$. With (*a*) MgBu$^{\gamma}$Cl or (*b*) $CMe_2Et{\cdot}MgCl$, $COMePr^{\beta}$ gives (*a*) $CHMePr^{\beta}{\cdot}OH$ (29%) and $COPr^{\beta}{\cdot}CH_2{\cdot}CMePr^{\beta}{\cdot}OH$ (VI)

(18%) (semicarbazone, m.p. 116°), *iso*-C_4H_{10} (63·6%) and -C_4H_8 (34·6%) with recovered $COMePr^{\beta}$ (46%) and C_2Me_6 (trace), and (*b*) $CHMePr^{\beta}\cdot OH$ (49%), $COPr^{\beta}\cdot CH{:}CMePr^{\beta}$ (**VII**) (35·6%), $COMePr^{\beta}$ (2%), and no gas. Dehydration of (**VI**) by boiling with I gives (**VII**), which with O_3 gives $COMePr^{\beta}$ and (?) $Pr^{\beta}CO\cdot CHO$. $CHEt_2\cdot CHBu^{\gamma}\cdot OH$, b.p. 123—124°/100 mm., gives the acetate, b.p. 90°/16 mm., and thence at 490—520° 70% of $CHEt_2{:}CHBu^{\gamma}$, b.p. 99°/20 mm., which with O_3 gives $Bu^{\gamma}CHO$ and $COEt_2$. With $MgBu^{\gamma}Cl$, (*a*) $(CH_2Bu^{\gamma})_2CH\cdot COCl$, (*b*) *n*-$C_{11}H_{23}\cdot COCl$, and (*c*) $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot COCl$ give (*a*) $(CH_2Bu^{\gamma})_2CH\cdot CH_2\cdot OH$ (60%), m.p. 44°, b.p. 108°/17 mm. (3 : 5-dinitrobenzoate, m.p. 101—102°), and $(CH_2Bu^{\gamma})_2CBu^{\gamma}\cdot OH$ (17%), b.p. 97—101°/5 mm. (3 : 5-*dinitrobenzoate*, m.p. 96—97°), (*b*) *n*-$C_{11}H_{23}\cdot CHBu^{\gamma}\cdot OH$ (67%), b.p. 149°/7 mm. [3 : 5-dinitrobenzoate, m.p. 64°; oxidised to *n*-$C_{11}H_{23}\cdot COBu^{\gamma}$, b.p. 155°/20 mm. (*semicarbazone*, m.p. 79°)], *n*-$C_{12}H_{25}\cdot OH$ (13·7%), and *n*-$C_{11}H_{23}\cdot CO_2CHBu^{\gamma}\cdot C_{11}H_{23}$-*n* (10·4%), m.p. 69—70°, and (*c*) $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CHO$ (62·5%), b.p. 101—104°/14 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 153°; oxidation by CrO_3 or air (less rapidly than that of PhCHO) gives the acid, m.p. 128°], and $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CH_2\cdot OH$ (19·7%), b.p. 113—114°/16 mm. Addition of $Pr^{\beta}CHO$ to $CMe_2Et\cdot MgCl$ gives 84% of $Bu^{\beta}OH$, and of $CMe_2Et\cdot MgCl$ to $Pr^{\beta}COCl$ gives 44% of $Pr^{\beta}CO_2Bu^{\beta}$. By addition to $CMe_2Et\cdot MgCl$, $CHEt_2\cdot COCl$ gives $CHEt_2\cdot CH_2\cdot OH$ (**VIII**) (74·5%) and $CHEt_2\cdot CH(OH)\cdot CMe_2Et$ (**IX**) (7·8%), b.p. 150—152°/150 mm. (*phenylurethane*, m.p. 71—72°; α-naphthylurethane, m.p. 85°), $CHEtBu^{\alpha}\cdot COCl$ gives $CHEtBu^{\alpha}\cdot OH$ (74·5%), b.p. 82°/20 mm., and $CHEtBu^{\alpha}\cdot CH(OH)\cdot CMe_2Et$ (15·7%), b.p. 125—137°/25 mm. (*phenylurethane*, m.p. 91—92°), $CHEt_2\cdot CHO$ gives (**VIII**) (67%) and (**IX**) (21%), $Bu^{\gamma}COCl$ gives $CH_2Bu^{\gamma}\cdot OH$ (97·5%), *n*-$C_{11}H_{23}\cdot COCl$ gives *n*-$C_{12}H_{25}\cdot OH$ (54·8%) and *n*-$C_{11}H_{23}\cdot CH(OH)\cdot CMe_2Et$, b.p. 190°/25 mm. (phenylurethane, m.p. 150—151°), $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot COCl$ gives $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CHO$ (**X**) (78%) and $CH_2Bu^{\gamma}\cdot CMeBu^{\gamma}\cdot CH_2\cdot OH$ (19%) [90% obtained from (**X**)], $CHPh{:}CH\cdot CHO$ gives only $CMe_2Et\cdot CHPh\cdot CH_2\cdot CHO$ (10%), b.p. 160—165°/24 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 130—131°), and mesityl oxide (**XI**) gives $COMe\cdot CH_2\cdot CMe_2\cdot CMe_2Et$ (**XII**) (16·2%), b.p. 118—120°/35 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 114°), a C_{11}-diene (8·3%), b.p. 75°/35 mm., $COMeBu^{\beta}$ (4%), and a trace of $CMe_2{:}CH\cdot CHMe\cdot OH$. (**XII**) yields $CHBr_3$ and $CMe_2Et\cdot CMe_2\cdot CH_2\cdot CO_2H$, m.p. 41—42° (*anilide*, m.p. 153°). With $MgBu^{\gamma}Cl$ in Bu_2O, AcCl gives $CHMeBu^{\gamma}\cdot OAc$ (11%), $COMeBu^{\gamma}$ (10%), $Bu^{\alpha}OAc$ (2%), (**XI**) (5%), and C_2Me_6. With $CMe_2Et\cdot MgCl$ in Et_2O, AcCl gives $CMe_2{:}CMe\cdot COMe$ (9%), b.p. 73—83°/56 mm. (semicarbazone, m.p. 185·5—187·5°), $COMe\cdot CMe_2Et$ (9%), and EtOAc (4%). $CH_2Bu^{\gamma}\cdot CHMe\cdot COCl$ and $MgBu^{\gamma}Cl$ give $CH_2Bu^{\gamma}\cdot CHMe\cdot CHBu^{\gamma}\cdot OH$ (67%), b.p. 102—106°/22 mm. [3 : 5-*dinitrobenzoate*; with CrO_3–AcOH gives (?) $CH_2Bu^{\gamma}\cdot CHMe\cdot COBu^{\gamma}$ (51%), b.p. 87—90°/16—18 mm., and 10% of $CH_2Bu^{\gamma}\cdot CHMe\cdot CO_2H$ (10%)], and $CH_2Bu^{\gamma}\cdot CHMe\cdot CH_2\cdot OH$ (21%), b.p. 78—80°/22 mm. (3 : 5-*dinitrobenzoate*, m.p. 72·5—73·5°; α-naphthylurethane, m.p. 70°; also obtained from $CH_2Bu^{\gamma}\cdot CHMe\cdot CO_2Et$ by Na–PhMe–EtOH and from $CH_2Bu^{\gamma}\cdot CHMe\cdot MgCl$ by CH_2O). Addition of $CH_2Ph\cdot COCl$ to $MgBu^{\gamma}Cl$ gives $CH_2Ph\cdot CHBu^{\gamma}\cdot OH$ (14·9%), b.p. 128°/20 mm. (*phenylurethane*, m.p. 82·5—85·5°), $CH_2Ph\cdot CO_2CHBu^{\gamma}\cdot CH_2Ph$ (20%), and $Ph\cdot[CH_2]_2\cdot OH$ (9·2%), but $CHPh_2\cdot COCl$ gives 67·5% of $CHPh_2\cdot CH_2\cdot OH$. $CH_2Bu^{\gamma}\cdot COCl$ and $MgBu^{\gamma}Cl$ give 48·5% of $CH_2Bu^{\gamma}\cdot CHBu^{\gamma}\cdot OH$ and 5% of $CH_2Bu^{\gamma}\cdot OH$. $Bu^{\gamma}COCl$ and $CH_2Bu^{\gamma}\cdot COCl$ with $MgBu^{\gamma}Cl$ give ~1% of RCHO. $CEt_3\cdot COCl$ with $MgBu^{\gamma}Cl$ gives 89·5% of $CEt_3\cdot CH_2\cdot OH$, b.p. 75°/13 mm. (α-naphthylurethane, m.p. 133—134°); $CBu^{\alpha}{}_3\cdot COCl$, b.p. 137—138°/12 mm., gives $CBu^{\alpha}{}_3\cdot CH_2\cdot OH$ (88·5%), b.p. 114—118°/3 mm. (phenylurethane, m.p. 77°). R. S. C.

II.—HOMOCYCLIC.

Synthesis of multi*cyclo*pentyls. G. E. Goheen (*J. Amer. Chem. Soc.*, 1941, **63**, 744—749).—*cyclo*Pentanol (prep. from the ketone in 94% yield by H_2–Raney Ni at 60—80°/1000—1600 lb.) and PBr_3 at 0° give the bromide (**I**), b.p. 136·7—137·7°. 1-Chloro-Δ^2-*cyclo*pentene (**II**) (prep. from the diene by dry HCl at −25°), b.p. 25—29°, and the Grignard reagent from (**I**) give 1-*cyclo*pentyl-Δ^2-*cyclo*pentene (**III**) (73·2%), b.p. 185—186°, which with fuming HBr at room temp. gives 3-*bromodicyclopentyl* (**IV**) (89·3%), b.p. 96°/1 mm., and with H_2–Raney Ni in EtOH at 100°/1800—1900 lb. gives di*cyclo*pentyl (62%), b.p. 190—190·5°/761·8 mm. The Grignard reagent from (**IV**) with (**II**) in Et_2O at 0° gives 44% of (**III**), 30% of 3-$\Delta^{2'}$-*cyclopentenyldicyclopentyl* (**V**), b.p. 140—141°/10 mm., and 14% of 3 : 3′-di(*cyclo*pentyl)di*cyclo*pentyl (**VI**), b.p. 183—185°/3 mm., 369—370°/761 mm. Addition of NaOEt–EtOH to *cyclo*pentanone at room temp. gives 36% of 2-*cyclo*pentylidene-, b.p. 102—103°/5 mm., and 46·3% of 2 : 5-di-(*cyclo*pentylidene)-*cyclo*pentanone (**VII**), m.p. 82°. H_2–Raney Ni in EtOH at 160—170°/1500 lb. converts (**VII**) into 1 : 3-di(*cyclo*pentyl)*cyclo*pentanol (87%), m.p. 68—69° [at 70—90° di(*cyclo*pentyl)*cyclo*pentanone is obtained], which with $ZnCl_2$ gives 1 : 3-*di*(cyclo*pentyl*)Δ^1-cyclo*pentene* (79·5%), b.p. 125—127°/1 mm., 300—301°/760 mm., reduced by H_2–Raney Ni in *iso*-C_6H_{14} at 135—140°/2200—2300 lb. to 3-cyclo*pentyldi*cyclo*pentyl* (**VIII**), b.p. 147—148°/12 mm., 296—297°/761 mm. An *isomeride*, b.p. 158°/16 mm., 293—294°/760 mm., of (**VIII**) is obtained by similar reduction of (**V**). (**VI**) is also obtained from the Grignard reagent of (**IV**) by AgBr. Physical consts. of the polycyclic hydrocarbons are recorded and discussed. R. S. C.

Determination of carotene in presence of lycopene.—See A., 1941, III, 407.

Palm oil carotenoids. I. Lipoid pigments from " Sherbro " palm oil.—See A., 1941, III, 315.

Copper [benzene] hydrogenation catalysts.—See A., 1941, I, 215.

Hydrogen fluoride as a condensing agent. XIV. Alkylation. J. H. Simons and G. C. Bassler (*J. Amer. Chem. Soc.*, 1941, **63**, 880—881; cf. A., 1941, II, 125).—Yields obtained from C_6H_6 and (*a*) CMe_2EtF, (*b*) C_5H_{10}–HF, or (*c*) C_6H_{10}–CMe_2EtF–HF, and from PhMe and *cyclo*hexene, *cyclo*hexanol, *cyclo*hexyl fluoride, chloride, bromide, or iodide in HF show that an aliphatic fluoride does not react in absence of HF, that olefines react at least as readily as do fluorides, that increase in the at. wt. of the halogen decreases the yield, and that alcohols react very readily. R. S. C.

Styrene substitutes and their polymerides. I. Methylstyrene and its polymeride. E. Matsui (*J. Soc. Chem. Ind. Japan*, 1941, **44**, 88—89B).—$(CH_2)_2O$–PhMe–$AlCl_3$ at ~10° afford β-*p*-tolylethyl alcohol, b.p. 231—232°/766 mm., 112—115°/8·5 mm., dehydrated by 10% KOH to *p*-methylstyrene, b.p. 67·5—68·5°/28 mm. Polymerides of the latter, hardened at 165—170° without catalyst for 11—30 hr., show little difference from polystyrene in appearance, although they are somewhat brittle. A. T. P.

Synthesis of *m*-di-β-phenylethylbenzene and its relationship to carcinogenic hydrocarbons. K. Sisido (*J. Soc. Chem. Ind. Japan*, 1941, **44**, 55—56B).—*m*-$C_6H_4(CH_2Br)_2$, CH_2PhCl, and Na refluxed in PhMe afford *m*-di-β-phenylethylbenzene, m.p. 56°. A. T. P.

Action of aluminium chloride on β-phenylethyl chloride. K. Sisido and S. Kato (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 450—451B).—The action of $AlCl_3$ on $Ph\cdot[CH_2]_2\cdot Cl$ (**I**) in CS_2 at 0° and subsequently at room temp. gives a red-violet elastic mass, m.p. >300°. Without solvent at 60—70° the product is a colourless, brittle mass, m.p. >300°. Both products are oxidised by $K_2Cr_2O_7$ and H_2SO_4 to *p*-$C_6H_4(CO_2H)_2$, suggesting the presence of long, linear chain mols. without branching or net formation. H. W.

Catalytic dehydrogenation of tetrahydronaphthalene and 1 : 2 : 3 : 4-tetrahydro-2-naphthol in the liquid phase. H. Adkins and W. A. Reid (*J. Amer. Chem. Soc.*, 1941, **63**, 741—744).—Liquid-phase dehydrogenation of tetrahydronaphthalene (**I**) (best prepared by H_2–Cu chromite at 200°/150—200 atm.) by Raney Ni at 350°/30—60 atm. (N_2) gives 78% of $C_{10}H_8$; at 300° a 35 : 25 : 40 equilibrium mixture of (**I**), dihydronaphthalene, and $C_{10}H_8$ is set up. (**I**) is stable in presence of Cu chromite at 350°. 1 : 2 : 3 : 4-Tetrahydro-2-naphthol (similarly prepared) is dehydrogenated by Raney Ni at 250°, giving mainly $C_{10}H_8$, and in presence of Cu chromite at 300° gives 70% of β-$C_{10}H_7\cdot OH$ and >1% of $C_{10}H_8$. C_2H_4 polymerises in steel at 350° giving products of b.p. >112°/2 mm., and decomposes in presence of Raney Ni at 300—350°; it is thus useless as H acceptor for the above dehydrogenations. R. S. C.

7-Methylcholanthrene and 5 : 1′-dimethyl-1 : 2-benzanthracene. W. E. Bachmann and S. R. Safir (*J. Amer. Chem. Soc.*, 1941, **63**, 855—857).—5-Keto-1′-methyl-5 : 6 : 7 : 8-tetrahydro-1 : 2-benzanthracene (**I**) and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give the 5-*OH*-compound (93%), m.p. 128·5—129°, which with HCl–$CaCl_2$–C_6H_6 at 5° gives the chloride, m.p. 127—127·5°, whence condensation with $CHNa(CO_2Et)_2$ in EtOH–C_6H_6 at, successively, room temp., 60°, and the b.p., followed by hydrolysis (KOH) and decarboxylation (190°), gives 1′-*methyl*-5 : 6 : 7 : 8-*tetrahydro*-1 : 2-*benzanthracene*-5-*acetic acid*, m.p. 145—145·5°. The derived (PCl_5–C_6H_6) chloride with $SnCl_4$–C_6H_6 at ~15° gives 97% of 1-*keto*-7-*methyl*-2a : 3 : 4 : 5-*tetrahydrocholanthrene*, m.p. 193·5—194°, reduced (Zn–Hg–PhMe–HCl–AcOH) to 7′-*methyl*-2a : 3 : 4 : 5-*tetrahydrocholanthrene* (99%), m.p. 90—98°, which with Pd–C–N_2 at 310° gives 7-*methylcholanthrene*, m.p. 147—148° (vac.; preheated at 135°) [*picrate*, m.p. 151—152° (vac.; preheated at 135°)]. MgMeI and (**I**) in Et_2O–C_6H_6 at 0° give an oily carbinol, which with Pd–C–N_2 at 310° gives 5 : 1′-*dimethyl*-1 : 2-*benzanthracene*, m.p. 106—107° [*picrate*, m.p. 150—150·5° (vac.)]. R. S. C.

***sec.* and *tert.* Amines from nitro-compounds.** W. S. Emerson and C. A. Uraneck (*J. Amer. Chem. Soc.*, 1941, **63**, 749—751).—Hydrogenation of $PhNO_2$ (1 mol.) and $Pr^{\alpha}CHO$ (1 mol.) in presence of a little $NHMe_3Cl$ and Raney Ni in 95% EtOH gives 63% of $NPhBu^{\alpha}_2$; 69% is obtained from a 1 : 3 mixture in presence of AcOH and PtO_2 in 95% EtOH. By the latter method, $NPhEt_2$ (70%), $NPhPr^{\alpha}_2$ (34%), and α-$C_{10}H_7$·NEt_2 (40%), b.p. 155—165°/30 mm. (*picrate*, m.p. 152—154°), and (from $MeNO_2$) $NMeEt_2$ (92%), $NMeBu^{\alpha}_2$ (56%), b.p. 155—163° (*hydrochloride*, m.p. 131—131·5°; *picrate*, m.p. 86—87·5°), and $NMePr^{\alpha}_2$ (45%), b.p. 110—122° (*picrate*, m.p. 92—93°), are obtained. Ketones give *sec.* amines, *e.g.*, $NHPhPr^{\beta}$ (53%) and $NHMePr^{\beta}$ (59%) from $COMe_2$ with $PhNO_2$ and $MeNO_2$, respectively. The reaction mechanism is probably: $RNO_2 \rightarrow {}^{+}NH_2R{\cdot}OH$ (+R′CHO) → $OH{\cdot}{}^{+}NHR{\cdot}CHR'{\cdot}OH \rightarrow OH{\cdot}N^{+}R{:}CHR' \rightarrow OH{\cdot}N^{+}HR{\cdot}CH_2R'$ (+R′CHO) → $OH{\cdot}CHR'{\cdot}N^{+}R(OH){\cdot}CH_2R' \rightarrow {}^{+}NHR(CH_2R')_2$. In conformity therewith, $CH_2Ph{\cdot}NPh{\cdot}OH$ and $Pr^{\alpha}CHO$ (2 mols.) give 38% of $NPhBu^{\alpha}{\cdot}CH_2Ph$, whereas only 3% thereof is obtained from $NHPh{\cdot}CH_2Ph$. R. S. C.

***sec.* and *tert.* Amines from azo-compounds.** W. S. Emerson, S. K. Reed, and R. R. Merner (*J. Amer. Chem. Soc.*, 1941, **63**, 751—752).—$(NPh{:})_2$ (1 mol.), RCHO (2·5 mols.), NaOAc, and H_2 (3—4 mols. absorbed)–Raney Ni in EtOH at 45 lb. give $NHPh{\cdot}CH_2R$, amines in which R = Pr^{α} (71%), *n*-hexyl (74%), and Ph (49%) being obtained. If $(NPh{:})_2$ carries an *o*- or *p*-activating group (OH, NMe_2), *tert.* amines are formed. Thus, *p*-$NMe_2{\cdot}C_6H_4{\cdot}N{:}NPh$ and $Pr^{\alpha}CHO$ give *p*-$NMe_2{\cdot}C_6H_4{\cdot}NBu^{\alpha}_2$ (76%), b.p. 150—175°/20 mm. (*picrate*, m.p. 121—122°), and $NHPhBu^{\alpha}$ (73%), *p*-$OH{\cdot}C_6H_4{\cdot}N{:}NPh$ gives *p*-$OH{\cdot}C_6H_4{\cdot}NBu^{\alpha}_2$ (46%) (*benzoate*, m.p. 232—233°), and 2 : 1-$OH{\cdot}C_{10}H_6{\cdot}N{:}NPh$ gives 1-*NN*-di-*n*-butylamino-β-naphthol (41%), unstable, m.p. 106—107° (*hydrochloride*, m.p. 225—227°). $(NHPh)_2$ is probably formed as intermediate. R. S. C.

Sulphonamide [derivatives]. II. Diphenyl derivatives. A. Novelli and J. C. Somaglino (*J. Amer. Chem. Soc.*, 1941, **63**, 854—855).—*p*′-$NO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$-*p* and Sn–HCl at >55° give the *p*′-NH_2-compound, m.p. 262—263° (decomp.). 4′-*Nitrodiphenyl*-4-*sulphonanilide*, m.p. 182—183°, gives similarly the 4′-NH_2-*anilide*, m.p. 182—183°. R. S. C.

Abnormal reaction in the Sommelet aldehyde synthesis. R. C. Fuson and J. J. Denton (*J. Amer. Chem. Soc.*, 1941, **63**, 654—656).—2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CH_2Cl$ (**I**) and $(CH_2)_6N_4$ in boiling $CHCl_3$ give the impure *salt*, $C_{16}H_{25}N_4Cl$, decomposed by boiling H_2O to NN′-*di*-(2 : 4 : 6-*trimethylbenzyl*)*methylenediamine* (**II**), m.p. 151·5—152°, and by boiling HCl–EtOH to 2 : 4 : 6-*trimethylbenzylamine hydrochloride* (**III**), m.p. 315° (decomp.). In boiling aq. HCl, (**II**) gives CH_2O and (**III**); in boiling AcCl and in BzCl at 120—150°, *acet*-, m.p. 186·5—187°, and *benz*-2 : 4 : 6-*trimethylbenzylamide*, m.p. 153·5—154°, respectively, are formed. With boiling aq. CH_2O and later boiling aq. NH_3–CH_2O, (**III**) gives (**II**). 2 : 4 : 6 : 1-$C_6H_2Me_3Br$ and CuCN in C_5H_5N at 220—230° give 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CN$, m.p. 50—52°, which with H_2–Raney Ni in EtOH at 150°/2200 lb. followed by HCl gives (**III**). *o*-$C_6H_4(CO)_2NK$ and (**I**) at 170—180° give *phthal*-2′ : 4′ : 6′-*trimethylbenzylimide*, m.p. 209·5—210°, hydrolysed to (**III**) (as hydrobromide) by boiling HBr–Ac_2O–AcOH. R. S. C.

***cis*-Azo-compounds. IV. Reactions with diphenylketen.** A. H. Cook and D. G. Jones (*J.C.S.*, 1941, 184—187).—*cis*-$(NPh{:})_2$ reacts rapidly with $CPh_2{:}CO$ (**I**) in light petroleum at room temp. to give 4-*keto*-1 : 2 : 3 : 3-*tetraphenyldimethylene*-1 : 2-*di*-*imine* (**II**), m.p. 175°, also obtained (more conveniently) by irradiation of a mixture of *trans*-$(NPh{:})_2$ and (**I**) in light petroleum, and (in small yield) from *trans*-$(NPh{:})_2$ and (**I**) at 125—130°/42 hr. in CO_2. Boiling 10% MeOH–NaOMe and (**II**) give *trans*-$(NPh{:})_2$; decomp. of (**II**) at 190° gives this and $NPh{:}CPh_2$. (**I**) when irradiated with the *trans*-azo-compounds, or, in the first two cases, when treated with the *cis*-azo-compounds in light petroleum, similarly yields 4-*keto*-3 : 3-*diphenyl*-1 : 2-*di*-m-*tolyl*-, m.p. 118°, -p-*tolyl*-, m.p. 172°, -o-*tolyl*-, m.p. 162°, and -β-*naphthyl*-*dimethylene*-1 : 2-*di*-*imine*, m.p. 222°. *p*-$NH_2{\cdot}C_6H_4{\cdot}N{:}NPh$ with (**I**) in C_6H_6 or with $CHPh_2{\cdot}COCl$ yields p-*diphenylacetamidoazobenzene*, m.p. 194°. *cis*- or (more slowly) *trans*-*p*-$C_6H_4Cl{\cdot}N_2{\cdot}CN$ with (**I**) in light petroleum yields 4-*keto*-1-*cyano*-2-p-*chlorophenyl*-3 : 3-*diphenyldimethylene*-1 : 2-*di*-*imine*, m.p. 121° (on one occasion the *cis*-cyanide afforded an isomeride, m.p. 266°), hydrolysed (aq. EtOH–NaOH) to α-β′-*cyano*-α′-p-*chlorophenylhydrazinodiphenylacetic acid*, m.p. 288° (decomp.). A. Li.

Positional influence of chlorine and of the nitro-group on colour of azo-dyes. Colorimetric evidence for the mesomeric and inductive effects.—See B., 1941, II, 138.

Catalytic decomposition of phenylhydrazine in presence of uracil. T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 761).—Uracil, thymine, and 4-methyluracil are unchanged in boiling $NHPh{\cdot}NH_2$, which is catalytically decomposed into NH_2Ph, C_6H_6, NH_3, and N_2. R. S. C.

Synthesis of phenol by partial-pressure evaporation.—See B., 1941, II, 135.

Alkylnitrophenols. W. H. Hartung and H. F. Koehler (*J. Amer. Chem. Soc.*, 1941, **63**, 872—873).—Condensation of PhOH with *sec.*-$C_6H_{13}{\cdot}OH$ and *tert.*-$C_5H_{17}{\cdot}OH$ by $ZnCl_2$ and treatment of the product in C_6H_6 with 1 : 1-HNO_3–H_2O at <5° gives x-*nitro*-y-sec.-*hexyl*-, b.p. 165—185°/2 mm., and -y-tert.-*octyl*-*phenol*, b.p. 157—168°/1 mm. Neither product is fungicidal. The product of nitration of *sec.*-hexyl-*m*-cresol decomposes when distilled. R. S. C.

Compounds related to natural œstrogens; γ-*cyclo*pentyl- and γ-2-methyl*cyclo*pentyl-δ-*p*-hydroxyphenyl-Δ$^{\gamma}$-hexene. H. Minlon (*Contr. Biol. Lab. Sci. Soc. China*, 1940, **15**, 17—27).—*cyclo*Pentyl bromide and $CNaEt(CO_2Et)_2$ in PhMe give Et_2 *cyclo*pentylethylmalonate, b.p. 146—152°/17 mm.; the free *acid*, m.p. 168—169°, when heated at 160—180° under reduced pressure affords α-*cyclo*pentylbutyric acid (**I**), b.p. 136—139°/15 mm. The chloride, b.p. 97—99°/15 mm., of (**I**) and PhOMe–$AlCl_3$–CS_2 at room temp. afford p-*methoxy*-α-cyclo*pentylbutyrophenone*, b.p. 132—133°/0·09 mm., which with MgEtBr yields δ-*cyclo*pentyl-γ-*p*-anisylhexan-γ-ol, b.p. 139—143°/0·5 mm., converted by PBr_3–$CHCl_3$ at 0° and then at room temp. into γ-cyclo*pentyl*-δ-p-*anisyl*-Δ$^{\gamma}$-*hexene*, b.p. 123—125°/0·3 mm., and thence (KOH–EtOH at 200°) into γ-cyclo*pentyl*-δ-p-*hydroxyphenyl*-Δ$^{\gamma}$-*hexene*, b.p. 127—129°/0·17 mm. 2-Methyl*cyclo*pentanone and $CHBrEt{\cdot}CO_2Et$–Zn–C_6H_6 afford Et α-(1-hydroxy-2-methyl*cyclo*pentyl)butyrate, b.p. 122—130°/16 mm., dehydrated by $SOCl_2$–C_5H_5N and then hydrolysed by 10% KOH–EtOH to α-(2-methyl-Δ^{1}-*cyclo*pentenyl)butyric acid, b.p. 148—152°/18 mm., hydrogenated (Pd; $COMe_2$) at room temp. and pressure to α-(2-*methyl*cyclo*pentyl*)*butyric acid*, b.p. 139—141°/16 mm. The chloride, b.p. 98—100°/16 mm., of the latter is converted into p-*methoxy*-α-2-*methyl*cyclo*pentylbutyrophenone*, b.p. 142—145°/0·12 mm., and thence (by MgEtBr) into the carbinol, b.p. 145—149°/0·3 mm., and (PBr_3) γ-2-*methyl*cyclo*pentyl*-δ-p-*anisyl*-Δ$^{\gamma}$-*hexene*, b.p. 124—127°/0·17 mm., demethylated to the corresponding p-*OH*-compound, b.p. 132—134°/0·1 mm. *p*-$OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CN$ (**II**) and MgEtBr yield β-keto-α-*p*-anisylbutan-α-ol, b.p. 173—175°/16 mm., converted by MgEtBr into α-*p*-anisyl-β-ethylbutane-αβ-diol, m.p. 78—79°, and thence (H_2SO_4) δ-*p*-anisylhexan-γ-one (*semicarbazone*, m.p. 131—132°; *oxime*, m.p. 114—115°), which does not react with Mg *cyclo*pentyl bromide (**III**). (**II**) and (**III**) afford cyclo*pentyl* α-*hydroxy*-p-*methoxybenzyl ketone*, m.p. 71—72° (*semicarbazone*, m.p. 162—163°), reduced by $SnCl_2$–HCl–EtOH at 100° (bath) to *cyclo*pentyl *p*-methoxybenzyl ketone,

m.p. 54—55° (*semicarbazone*, m.p. 151—152°), which could not be ethylated. A. T. P.

2-Methyl-1 : 4-naphthaquinol hydrogen succinate. R. Baltzly and J. S. Buck (*J. Amer. Chem. Soc.*, 1941, **63**, 882). —2-Methyl-1 : 4-naphthaquinol (1 mol.) and $(CH_2{\cdot}CO)_2O$ (4 mols.) at 140° give the (mono-)*H succinate*, m.p. 176—178°, showing vitamin-*K* activity in doses of 2 μg. R. S. C.

Derivatives of 4 : 4'-diaminodiphenyl sulphone.—See B., 1941, III, 132.

Synthesis of unsaturated substances from β-ionone and substituted vinylacetylenes. A. F. Thompson, jun., N. A. Milas, and I. Rovno (*J. Amer. Chem. Soc.*, 1941, **63**, 752—755).—Addition of β-ionone (**I**) to $CH_2{:}CH{\cdot}C{\equiv}C{\cdot}MgBr$ in boiling Et_2O gives 59% of α-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-γ-*methyl*-$\Delta^{\alpha\zeta}$-n-*heptadien*-Δ^{δ}-*inen*-γ-*ol* (**II**), b.p. 155—160°/2 mm., obtained also in 11—20% yield from $CH_2{:}CH{\cdot}C{\equiv}CH$ and (**I**) by $CMe_2Et{\cdot}OK$–$CMe_2Et{\cdot}OH$ at −10°. With tetrahydroionone both methods give 80% of η-2 : 6 : 6-*trimethyl*-cyclo*hexyl*-ε-*methyl*-Δ^{α}-*hepten*-Δ^{γ}-*inen*-ε-*ol* (**III**), b.p. 155—160°/2 mm. H_2–Pd–$CaCO_3$ reduces (**II**) and (**III**) in abs. EtOH to α-2 : 6 : 6-trimethyl-Δ^1-*cyclo*hexenyl-γ-methyl-$\Delta^{\alpha\delta\zeta}$-heptatrien-$\gamma$-ol (**IV**), b.p. 155—160°/2 mm., and η-2 : 6 : 6-trimethyl*cyclo*hexyl-ε-methyl-$\Delta^{\alpha\gamma}$-heptadien-ε-ol, b.p. 150—155°/2 mm., respectively, both of which are further hydrogenated (PtO_2) to α-2 : 6 : 6-*trimethyl*cyclo*hexyl*-γ-*methyl*-n-*heptan*-γ-*ol*, b.p. 145—150°/2 mm. $CH{:}C{\cdot}CMe{:}CH_2$ and $CH{:}C{\cdot}CMe{:}CHMe$ give similarly α-2 : 6 : 6-*trimethyl*-Δ^1-cyclo*hexenyl*-$\gamma\zeta$-*dimethyl*-$\Delta^{\alpha\zeta}$-n-*hepta*-, b.p. 165—170°/2 mm., and -*octa*-*dien*-Δ^{δ}-*inen*-γ-*ol*, b.p. 170—175°/2 mm., α-2 : 6 : 6-trimethyl-Δ^1-*cyclo*hexenyl-$\gamma\zeta$-dimethyl-$\Delta^{\alpha\delta}$-hepta- (**V**), b.p. 165—170°/2 mm., and -octa-trien-γ-ol (**VI**), b.p. 170—175°/2 mm., η-2 : 6 : 6-*trimethyl*cyclo*hexyl*-$\beta\varepsilon$-*dimethyl*-Δ^{α}-*hepten*-Δ^{γ}-*inen*-ε-*ol*, b.p. 165—170°/2 mm., θ-2 : 6 : 6-*trimethyl*cyclo*hexyl*-$\gamma\zeta$-*dimethyl*-Δ^{β}-*octen*-Δ^{δ}-*inen*-ζ-*ol*, b.p. 170—175°/2 mm., η-2 : 6 : 6-trimethyl*cyclo*hexyl-$\beta\varepsilon$-dimethyl-$\Delta^{\alpha\gamma}$-heptadien-ε-ol, b.p. 160—165°/2 mm., θ-2 : 6 : 6-trimethyl*cyclo*hexyl-$\gamma\zeta$-dimethyl-$\Delta^{\beta\delta}$-octadien-ζ-ol, b.p. 165—170°/2 mm., α-2 : 6 : 6-*trimethyl*cyclo*hexyl*-$\gamma\zeta$-*dimethyl*-n-*heptan*-γ-*ol*, b.p. 155—160°/2 mm., and -*n*-octan-γ-ol, b.p. 160—165°/2 mm. (**IV**), (**V**), and (**VI**) have no vitamin-*A* activity. Attempts to rearrange them to primary alcohols failed. R. S. C.

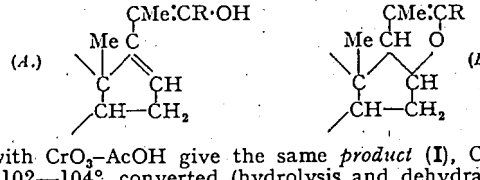
Sponge sterol. A. Mazur (*J. Amer. Chem. Soc.*, 1941, **63**, 883—884).—*Spongila lacustris* yields mixed sterols, whence, by acetylation and adsorption on Al_2O_3, a *sterol*, $C_{29}H_{50}O$, m.p. 136·5—137°, $[\alpha]_D$ −41·8° in $CHCl_3$ (*acetate*, m.p. 137°, $[\alpha]_D$ −47·6° in $CHCl_3$; *benzoate*, m.p. 137·5°, $[\alpha]_D$ −17·1° in $CHCl_3$; 3 : 5-*dinitrobenzoate*, m.p. 200°, $[\alpha]_D$ −18·3° in $CHCl_3$; hydrogenated to stigmastanol), and another sterol (impure) are obtained. R. S. C.

Lanosterol. II. Oxidation of lanosterol with chromic acid. III. Action of selenium dioxide and of perbenzoic acid on lanosterol. L. J. Bellamy and C. Dorée (*J.C.S.*, 1941, 172—176, 176—181; cf. A., 1936, 1505).—II. Lanosterol (**I**) with CrO_3 in H_2O–AcOH–C_6H_6 at room temp. gives 40% of lanostenone (**II**), and an isomeride, *lanostenone*-B, m.p. 78° (2 : 4-dinitrophenylhydrazone, m.p. 191°; tetrahydrocarbazole derivative, m.p. 178°, from $NHPh{\cdot}NH_2$), reduced (Na + EtOH) to (**I**). (**II**) is reduced (Na + EtOH) to α-dihydrolanosterol, or $[Al(OPr^{\beta})_3$ in $Pr^{\beta}OH]$ to lanosterol-*E*, m.p. 143° (*acetate*, m.p. 164°). Vigorous oxidation (CrO_3) of (**I**) gives an acid, $C_{25}H_{46}O_2$, m.p. 81—82° (Et ester, m.p. 64°), unaffected by Br, H_2 (Pd–C), or Bz_2O_2H. Lanosteryl acetate (**III**) with CrO_3–H_2O–AcOH yields the acetate (**IV**), m.p. 164°, $[\alpha]_D^{20}$ +44° in $CHCl_3$, of lanosterol-*D*, m.p. 145°, oxidised [as for (**I**)] to lanostenone-*D*, m.p. 105° (tetrahydrocarbazole derivative, m.p. 128°). Hydrogenation (Pd–C, AcOH) of (**IV**) yields dihydrolanosteryl-*D* acetate, m.p. 218°. (**I**) is unaffected by $Al(OBu^{\nu})_3$ in $COMe_2$.

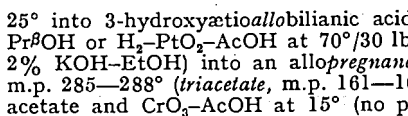
III. (**III**) with SeO_2 in boiling EtOH yields the *monoacetate*, m.p. 110°, of a *diol*, $C_{30}H_{50}O_2$, m.p. 143—144° (*diacetate*, m.p. 132°) (with a small amount of an isomeric *diol*, m.p. 152°). (**III**) must therefore contain a CH_2 group adjacent to the active double linking. α-Dihydrolanosteryl acetate with SeO_2 in boiling AcOH yields the *acetate* (**V**), m.p. 167°, of γ-*lanosterol* (? α-dihydroagnosterol), m.p. 141°, oxidised (CrO_3) to γ-*lanostenone*, m.p. 124° (tetrahydrocarbazole derivative, m.p. 228°). Hydrogenation (Pd–C, AcOH) of (**V**) yields α-dihydrolanosteryl acetate. (**III**) with Bz_2O_2H in $CHCl_3$ at 0° yields an oxide, m.p. 185°, hydrolysed (aq. EtOH–HCl) to *lanostenetriol*, m.p. 130° (*diacetate*, m.p. 104°). (**II**) with Bz_2O_2H affords an *oxide*, m.p. 92°, converted by EtOH–HCl into *dehydrolanostenone*, $C_{30}H_{46}O$, m.p. 126° (tetrahydrocarbazole derivative, m.p. 228°; oxime, m.p. 183°), which is hydrogenated (Pd–C) to α-*iso*dihydroagnostenone, m.p. 124° (tetrahydrocarbazole derivative, m.p. 202°; oxime, m.p. 164°). The significance of these results is discussed; (**I**) is a tetracyclic, doubly unsaturated alcohol probably related to the triterpenes. A. Li.

Sterols. CXIX. Sapogenins. XLVII. Pregnanetriols from ψ-sapogenins. R. E. Marker, D. L. Turner, R. B. Wagner, P. R. Ulshafer, H. M. Crooks, jun., and E. L. Wittle (*J. Amer. Chem. Soc.*, 1941, **63**, 779—782).—ψ-Tigogenin with CrO_3–AcOH at 28° gives (cf. following abstract) a non-cryst. product, converted by H_2–PtO_2–AcOH and subsequent hydrolysis into allo*pregnane*-3(β) : 16 : 20(β)-*triol*, m.p. 286—288°, and by acid or alkali into $CO_2H{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}CO_2H$ and Δ^{16}-*allo*pregnene-3 : 20-dione. ψ-Sarsasapogenin and its diacetate or dihydro-ψ-sarsasapogenin diacetate with CrO_3–AcOH at 20—30°, followed by H_2–PtO_2 and then KOH–EtOH, give *pregnane*-3(β) : 16 : 20(β)-*triol*, m.p. 236—240° (*triacetate*, m.p. 145—148°). *epi*-ψ-Sarsasapogenin diacetate gives similarly *pregnane*-3(α) : 16 : 20(β)-*triol*, m.p. 203—206° (*triacetate*, m.p. 175—177°). *epi*-ψ-Tigogenin diacetate gives allo*pregnane*-3(α) : 16 : 20(β)-*triol*, m.p. 263—265° (*triacetate*, m.p. 181°). ψ-Deoxysarsasapogenin acetate or dihydro-ψ-deoxysarsasapogenin gives Δ^{16}-*pregnen*-20-*one*, m.p. 129—131°, identified by hydrogenation (H_2–Pd–$BaSO_4$–EtOH–Et_2O) to pregnan-20-one. Δ^{16}-*allo*Pregnen-3(β)-ol-20-one with $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ and then 8% KOH–MeOH gives Δ^{16}-allo*pregnene*-3(β) : 20(β)-*diol*, m.p. 188—190° (*diacetate*, m.p. 102—104°), hydrogenated (PtO_2 in Et_2O–MeOH containing a little AcOH; 45 lb.) to *allo*pregnane-3(β) : 20(β)-diol (**I**). Similar reduction of $\Delta^{5:16}$-pregnadien-3(β)-ol-20-one gives $\Delta^{5:16}$-*pregnadiene*-3(β) : 20(β)-*diol*, m.p. 169—171° (*diacetate*, m.p. 121°), hydrogenated to (**I**). R. S. C.

Sterols. CXVII. Sapogenins. XLVI. Structure of ψ-sapogenins. R. E. Marker, D. L. Turner, R. B. Wagner, P. R. Ulshafer, H. M. Crooks, jun., and E. L. Wittle (*J. Amer. Chem. Soc.*, 1941, **63**, 774—777).—ψ-Sapogenins probably exist in tautomeric forms (*A*) and (*B*), the former accounting for formation of diketo-acids and certain other oxidations, and the latter accounting for the following reactions. Diacetates of dihydro-ψ-tigogenin at 30° and of ψ-tigogenin at



15° with CrO_3–AcOH give the same *product* (**I**), $C_{31}H_{48}O_7$, m.p. 102—104°, converted (hydrolysis and dehydration) by boiling 2% KOH–EtOH, K_2CO_3–EtOH, or 10% HCl–EtOH into Δ^{16}-*allo*pregnen-3(β)-ol-20-one, by Na–$Pr^{\beta}OH$ into *allo*pregnane-3(β) : 20(α)-diol (**II**), by CrO_3 in 90% AcOH at



25° into 3-hydroxyætio*allo*bilianic acid, and by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ or H_2–PtO_2–AcOH at 70°/30 lb. (later hydrolysis by 2% KOH–EtOH) into an allo*pregnane*-3 : 16 : 20-*triol* (**III**), m.p. 285—288° (*triacetate*, m.p. 161—163°). ψ-Diosgenin diacetate and CrO_3–AcOH at 15° (no protection of the C:C) give similarly a *product*, $C_{31}H_{46}O_7$, m.p. 84—86°, and thence by acid or alkali $\Delta^{5:16}$-pregnadien-3(β)-ol-20-one, by Na–$Pr^{\beta}OH$ a product converted by H_2–PtO_2–AcOH into (**II**), by H_2–PtO_2 in Et_2O at 30 lb. into (**I**), by H_2–PtO_2 in AcOH at 70°/45 lb. into (**III**), and by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ followed by hydrolysis (2% MeOH–KOH) into a Δ^5-*pregnene*-3 : 16 : 20-*triol*, m.p. 281—285° (*triacetate*, m.p. 143°), which with H_2–PtO_2–AcOH also gives (**III**). R. S. C.

Alkamine esters of di*cyclo*hexylacetic and related acids.—See B., 1941, III, 133.

Preparation of benzoic acid of high purity. F. W. Schwab and E. Wichers (*J. Res. Nat. Bur. Stand.*, 1940, **25**, 747—

757).—Fractional distillation in a vac., recrystallisation from H_2O or pure C_6H_6, fractional freezing, oxidation of purified PhMe followed by recrystallisation from H_2O, and hydrolysis of purified BzCl have been compared as methods for producing pure BzOH. Eight recrystallisations from C_6H_6, fractional freezing, and hydrolysis of BzCl each yield products of purity $<99{\cdot}999\%$. The f.p. of pure BzOH is assigned tentatively as $122{\cdot}36\pm0{\cdot}01°$. J. W. S.

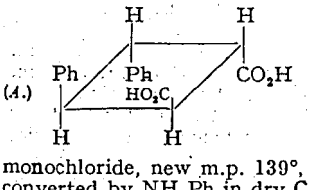
Hippuric acid derivatives.—See B., 1941, III, 133.

Preparation of lower monoalkylaminoethyl aminobenzoates.—See B., 1941, III, 132.

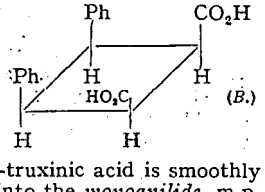
Preparation of hydroxynaphthoic acids. J. Cason (*J. Amer. Chem. Soc.*, 1941, **63**, 828—832).—1 : 3 : 8-$NH_2{\cdot}C_{10}H_5(SO_3H)_2$, Zn dust, and a little *n*-$C_6H_{13}{\cdot}CHMe{\cdot}OH$ in boiling aq. NaOH give 1 : 3-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3Na$ (81—87%), converted by KCN at ~500° into 1 : 3-$NH_2{\cdot}C_{10}H_6{\cdot}CN$ (10—13%), new m.p. 125·5—126°, which in 70% H_2SO_4–AcOH (1 : 4) gives 4 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}CO_2H$ (**I**), new m.p. 215—216°, and in 10% H_2SO_4 at $195\pm5°$ gives 4 : 2-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$ (90·5%), m.p. 225—226° (lit. 182—183°) [acetate, m.p. 211·5—212·5° (lit. 168°)], also obtained with difficulty from (**I**). *4-Acetoxy-2-naphthoyl chloride* (prep. by PCl_5), m.p. 96—98°, remelting at 99·0—99·5°, with H_2–Pd–$BaSO_4$ and a little S-quinoline in boiling xylene gives *4-acetoxy-2-naphthaldehyde* (51%), m.p. 113·2—114·2° [*semicarbazone*, m.p. ~230° (decomp.), obtained in 73·5% yield from the crude reaction product; Wolff–Kishner reduction fails], hydrolysed by boiling N-H_2SO_4 to *4-hydroxy-2-naphthaldehyde*, m.p. 169·5—170°, which with H_2–Cu chromite in abs. EtOH at 140° yields 3 : 1-$C_{10}H_6Me{\cdot}OH$, m.p. 87—90°, remelts at 91°. 1 : 6-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3Na$ gives similarly 5 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}CN$ (**I**) (~10%), new m.p. 143·5—144°, and thence 5 : 2-$NH_2{\cdot}C_{10}H_6{\cdot}CO_2H$ (**II**), new m.p. 234—236° (decomp.) [Ac derivative, m.p. 291—292° (gas)]. 10% H_2SO_4 and (**I**) at $220\pm5°$ give 67% of 5 : 2-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$, new m.p. 215—216° (acetate, new m.p. 215—216°), but at 180° give (**II**). 2 : 6-$NH_2{\cdot}C_{10}H_6{\cdot}SO_3Na$ gives *6-amino-2-naphthonitrile* (1·5%), m.p. 199·0—199·5°, and thence 6 : 2-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$, new m.p. 243—244° (acetate, new m.p. 223—224°). 5 : 1-$OH{\cdot}C_{10}H_6{\cdot}CO_2H$, new m.p. 237—240° (decomp.) (acetate, m.p. 205—206°), is similarly obtained (53—57%). M.p. are corr. R. S. C.

Fluoranthenecarboxylic acids.—See B., 1941, II, 137.

Spatial structure of two new diphenylcyclobutanedicarboxylic acids; μ- and ω-truxinic acids. M. M. Schemjakin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 199—201; cf. A., 1940, II, 87).—The monoanilide of μ-truxinic acid is unchanged when heated at 270° or boiled with 10% HCl for 2·5 hr.; it is readily hydrolysed by boiling 5% KOH–H_2O. The



(*A*.)



(*B*.)

monochloride, new m.p. 139°, of ω-truxinic acid is smoothly converted by NH_2Ph in dry C_6H_6 into the *monoanilide*, m.p. 108—111° (decomp.) and 169—173° after re-solidification. It is readily hydrolysed by boiling aq. KOH and is converted when heated alone or with 10% HCl into the *anil*, m.p. 179°. μ- and ω-Truxinic acid are (*A*) and (*B*) respectively. H. W.

Properties of μ-truxinic acid. M. M. Schemjakin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 202—205).—The most characteristic property of μ-truxinic acid (**I**) is the difference in character between the two CO_2H. (**I**), m.p. 196°, dissolves in aq. Na_2CO_3 with formation of a Na H salt and with NH_3 in Et_2O gives the *NH*$_4$*H* salt, m.p. 150—160° (decomp.). (**I**) is unchanged by boiling Ac_2O. The Me ester, m.p. 196° (A., 1940, II, 87), is the Me H ester (**II**), since it is obtained by short treatment of the monochloride (**III**) with MeOH and is converted by MeOH–H_2SO_4 or NaOH–Me_2SO_4 into the Me_2 ester (**IV**), m.p. 183°. (**I**) is isomerised to ω-truxinic acid (**V**) at 240—245°. (**II**), (**III**), (**IV**), and μ-truxinmonoanilide (**VI**) are partly transformed into (**V**) when boiled with 5—10% aq. NaOH until dissolution is complete; with boiling 10% HCl, (**V**) is the sole product [except from (**VI**), which hydrolyses only with difficulty]. (**III**) and NaOMe in boiling MeOH afford Me_2 ω-truxinate, m.p. 133°, also obtained with the β-ester from (**IV**) at 260°. H. W.

Preparation of symmetrical diaryls by the action of reducing agents on diazotised amines. Reducing agents. E. R. Atkinson, H. J. Lawler, J. C. Heath, E. H. Kimball, and E. R. Read (*J. Amer. Chem. Soc.*, 1941, **63**, 730—733).—Diphenic acid is obtained in 90% yield from *o*-$CO_2H{\cdot}C_6H_4{\cdot}N_2Cl$ by Cu_2O–NH_3 (<1 atom of Cu). CuCl–HCl gives *o*-$C_6H_4Cl{\cdot}CO_2H$. Cu^{II}–NH_3 gives no Ph_2 derivative. R. S. C.

Lactones of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1941, III, 133.

Condensation of malonanilic acid with aldehydes. II. With *o*-, *m*-, and *p*-hydroxybenzaldehyde. III. With *o*-, *m*-, and *p*-nitrobenzaldehyde. P. I. Ittyerah and K. C. Pandya (*Proc. Indian Acad. Sci.*, 1941, **13, A**, 119—121, 122—125; cf. Mehra *et al.*, A., 1938, II, 365; 1939, II, 478).—II. Malonanilic acid (**I**) and *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ at 100° (not at 60°) yield coumarin-3-carboxylanilide, m.p. 247°, also obtained in presence of a base. (**I**) and *m*- or *p*-$OH{\cdot}C_6H_4{\cdot}CHO$ afford m-, m.p. 209°, or p-*hydroxybenzylidenemalonanilic acid*, m.p. 239—240° (in 52% and 18% yield). *Benzylidenemalonanilic acid*, m.p. 238°, is obtained in 86% yield from PhCHO and (**I**) at 100°.

III. (**I**) and *o*-, *m*-, or *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ at 100° give a mixture of substituted cinnamanilide and benzylidenemalonanilic acid, reaction proceeding least rapidly with the *o*-compound, probably owing to the presence of a H bond. p-, m.p. 240° (decomp.) (*Ag* salt, decomp. 231°), and m-*nitrobenzylidenemalonanilic acid*, m.p. 226° (decomp.) (*Ag* salt, decomp. 211°), are new. H. W.

Interconversion of mixed benzoins. R. P. Barnes and V. J. Tulane (*J. Amer. Chem. Soc.*, 1941, **63**, 867—868).—Both *p*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CHPh{\cdot}OAc$ and *αβ-diacetoxy-4-methoxystilbene*, m.p. 127°, are obtained by boiling Ac_2O–KOAc from *p*-$OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}COPh$, *p*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CHPh{\cdot}OH$ (**I**), or *p*-$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CHPhBr$. The enediol is an intermediate in the last two cases, (**I**) being the stable form favoured by resonance. R. S. C.

Δ²-*cyclo*Hexenone and related substances. F. C. Whitmore and G. W. Pedlow, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 758—760).—Addition of MgRX to Δ²-*cyclo*hexenone (**I**) results in 1 : 2- and 1 : 4-addition, reduction, and formation of complex products in the following proportions: R = Me, X = Br 38, 15, 0, 18, Et, Br 52, 24, 0, 13, Pr^{β}, Cl, 10, 44, 12, 16, and Bu^{γ}, Cl 0, 70, 0, 14. *iso*Phorone with MgMeBr and MgEtBr gives no 1 : 4-addition and only 8% with $MgPr^{\beta}Br$. (**I**) and its 2 + 3-Me derivative are prepared (yields 37 and 2 + 20%, respectively) from *cyclo*hexene and 1-methyl*cyclo*hexene, respectively, by CrO_3–AcOH. Compounds of the following probable constitution are described: 1-methyl-, b.p. 63—65°/20 mm. {and thence by $CuSO_4$ a diene, b.p. 106·5—107°/738 mm. [maleic anhydride adduct, m.p. 65—66°; with $KMnO_4$ gives $(CH_2(CO_2H)_2)$]}, and 1-*iso*propyl-Δ²-*cyclo*hexenol, b.p. 72—74°/13 mm.; 3 : 3 : 5 : 5-tetramethyl-, m.p. 37—38°, and 3 : 5 : 5-trimethyl-1-ethyl-Δ²-*cyclo*hexenol, m.p. 49—50°; 3 : 5 : 5-trimethyl-3-*iso*propyl-*cyclo*hexanone, b.p. 115°/20 mm. [semicarbazone, m.p. 199—200° (decomp.); 2 : 4-dinitrophenylhydrazone, m.p. 154—155°]; 3-*tert.*-butyl*cyclo*hexanone, b.p. 96—98°/20 mm. [semicarbazone, m.p. 207—208° (decomp.); 2 : 4-dinitrophenylhydrazone, m.p. 158—159°]. A polymeric product was obtained from (**I**) and Δ¹·³-*cyclo*hexadiene. R. S. C.

Reaction of *cyclo*pentadiene and keten. B. T. Brooks and G. Wilbert (*J. Amer. Chem. Soc.*, 1941, **63**, 870—871).—Contrary to Smith *et al.* (A., 1939, II, 116), keten and *cyclo*pentadiene in PhMe at 100° give Δ²-*dicyclo*[0, 2, 3]*heptene*-6 (or 7)-*one*, b.p. 157·5—159° (*semicarbazone*, m.p. 222°), hydrogenated (Pd–aq. EtOH) to *dicyclo*[0, 2, 3]heptan-6-one, b.p. 164—165° (semicarbazone, m.p. 216°), which with boiling 1 : 1 conc. HNO_3–H_2O gives glutaric acid. R. S. C.

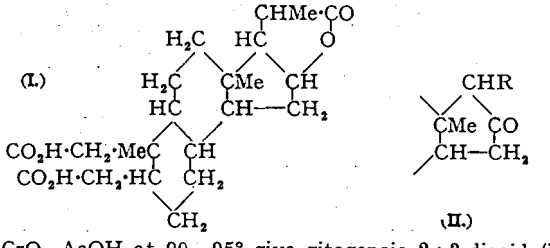
Naphthalene series. VIII. Preparation and properties of 2 : 4-dipropionyl- and 4-acetyl-2-propionyl-1-naphthol. IX. Properties of 4-propionyl-1-naphthol and preparation of 4-propyl-1-naphthol. R. D. Desai and A. Hamid (*Proc. Indian Acad. Sci.*, 1941, **13, A**, 126—131, 132—136).—VIII. Gradual addition of EtCOCl to 2 : 1-$COEt{\cdot}C_{10}H_6{\cdot}OH$ and anhyd. $ZnCl_2$ in $PhNO_2$ gives an almost quant. yield of 2 : 4-*dipropionyl-1-naphthol* (**I**), m.p. 103°, less advantageously obtained by use of $AlCl_3$ and (**V**) (below). (**I**) does not give

a picrate. It is converted by Br in glacial AcOH into *4-propionyl-2-α-bromopropionyl-1-naphthol*, m.p. 100°, converted by hot 5% NaOH into a neutral *compound*, $C_{16}H_{14}O_3$, m.p. 254°, and an acidic *product*, $C_{16}H_{14}O_3$, m.p. 133°. (I) with HNO_3 (*d* 1·5) (1 mol.) in cold, glacial AcOH gives 4-nitro-2-propionyl- (II), m.p. 162°, 2-nitro-4-propionyl- (III), m.p. 100°, and 2 : 4-dinitro-1-naphthol (IV), m.p. 138°; with 2 mols. of acid the products are (III) and (IV). (I) and anhyd. $ZnCl_2$ in boiling AcOH or $EtCO_2H$ give 2 : 1-COEt·$C_{10}H_6$·OH. (I) is converted by Ac_2O and anhyd. NaOAc at 170—180° into *6-propionyl-2 : 3-dimethyl-1 : 4-α-naphthapyrone*, m.p. 168°, hydrolysed by boiling 5% NaOH to *1-hydroxy-4-propionyl-2-naphthoic acid*, m.p. 205°; this passes above its m.p. into 4 : 1-COEt·$C_{10}H_6$·OH (V), m.p. 188°, and is reduced (Clemmensen) to *1-hydroxy-4-propyl-2-naphthoic acid*, m.p. 174°, decarboxylated to 4 : 1-$C_{10}H_6Pr^{\alpha}$·OH. 2 : 1-COEt·$C_{10}H_6$·OH, AcCl, and anhyd. $ZnCl_2$ in $PhNO_2$, or EtCOCl, 4 : 1-$C_{10}H_6Ac$·OH, and $AlCl_3$ give *4-acetyl-2-propionyl-1-naphthol* (VI), m.p. 142°, in 80% or 75% yield. (VI) does not form a picrate. When heated with $ZnCl_2$ in AcOH or $EtCO_2H$ it affords 2 : 1-COEt·$C_{10}H_6$·OH. (VI) and Br in $CHCl_3$ yield *4-bromoacetyl-2-propionyl-1-naphthol*, m.p. 158°, converted by 5% NaOH or NaOMe into an acidic *product*, $C_{15}H_{14}O_4$, m.p. 108°. With 1 mol. of fuming HNO_3 in cooled glacial AcOH, (VI) gives (II), (IV), and 2 : 1-NO_2·$C_{10}H_6$·OH. (VI) is converted by Kostanecki's reaction into *6-acetyl-2 : 3-dimethyl-1 : 4-α-naphthapyrone*, m.p. 189°, hydrolysed in alkaline solution to *1-hydroxy-4-acetyl-2-naphthoic acid*, m.p. 219—220°, which passes at 200° into 4 : 1-$C_{10}H_6Ac$·OH.

IX. (V), m.p. 188°, is best obtained by addition of EtCOCl to α-$C_{10}H_7$·OH and anhyd. $ZnCl_2$ in well-cooled $PhNO_2$; inferior results are obtained with $(EtCO)_2O$ or $AlCl_3$. (V) gives an *acetate*, m.p. 92°, a *picrate*, m.p. 158°, and a *semicarbazone*, m.p. 223°. $ZnCl_2$ in glacial AcOH or $EtCO_2H$ transforms (V) into 4 : 2 : 1-COEt·$C_{10}H_5Ac$·OH, 2 : 1-$C_{10}H_6Ac$·OH, α-$C_{10}H_7$·OH, and 2 : 1-COEt·$C_{10}H_6$·OH. With differing amounts of Br in $CHCl_3$ (V) gives *2-bromo-4-propionyl-*, m.p. 111°, and *2-bromo-4-α-bromopropionyl-*, m.p. 132°, *-1-naphthol*. With 1 mol. of fuming HNO_3, (V) yields *2-nitro-4-propionyl-1-naphthol*, m.p. 100°, accompanied by 2 : 1-NO_2·$C_{10}H_6$·OH and (IV), which is the sole product when 2 mols. of HNO_3 are used. (V) is reduced (Clemmensen) to *4-propyl-1-naphthol* (VII), b.p. 150°/6 mm. (*picrate*, m.p. 138°), and (?) *4-propyl-1 : 2 : 3 : 4-tetrahydro-1-naphthol*, b.p. 126—128°/6 mm. (VII) and $ZnCl_2$ in boiling AcOH afford *2-acetyl-4-propyl-1-naphthol*, m.p. 185°. (VII) couples with PhN_2Cl to *2-benzeneazo-4-propyl-1-naphthol*, m.p. 186°, and *4-propyl-1 : 2-naphthaquinone-2-phenylhydrazone*, m.p. 150°.

H. W.

Sterols. CXIV. Sapogenins. XLIII. Oxidation products from tigogenin. R. E. Marker, D. L. Turner, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1941, **63**, 763—767).—Marker's formula for the side-chain of steroidal sapogenins is supported by the following reactions. Gitogenin lactone and CrO_3 in 90% AcOH at 25° or tigogenone and AcOH–HNO_3 (*d* 1·5) at 90° give the lactone 2 : 3-diacid (I), m.p. 244—245° (Windaus *et al.*, A., 1925, i, 1438; +0·5H_2O, m.p. 238°). Tigogenin



and CrO_3–AcOH at 90—95° give gitogenoic 2 : 3-diacid (II) (R = ·CHMe·CO·$[CH_2]_2$·CHMe·CO_2H), +0·5H_2O, m.p. 216—219° (also obtained from gitogenic acid) (with some 3-dehydrotigogenin lactone), which with fuming HNO_3 at room temp. gives 16-ketobisnor*alloiso*lithobilianic acid (II) (R = CHMe·CO_2H) (cf. *loc. cit.*), m.p. 295—298° (decomp.), reduced by H_2–PtO_2–EtOH–Et_2O to (I). Dihydrotigogenin diacetate and CrO_3 in AcOH at 90—95° give tigogenin lactone, 3-dehydrotigogenoic acid, and *3-hydroxyætio*allobilianic *acid* (III), m.p. 244—247° (decomp.) (oxidised by CrO_3 to the known 3-CO-acid). Tigogenoic acid (IV) with NH_2OH,HCl and KOAc in MeOH at 130° gives a *dioxime*, brown at 230°, decomp. 250° (gas), with KOH in boiling aq. EtOH gives *anhydrotigogenoic acid*, m.p. 256—258°, and with H_2–PtO_2 at 45 lb. in AcOH gives *anhydrotetrahydrotigogenoic acid*, m.p. 203—205°, also obtained by oxidation (CrO_3–AcOH) of dihydrotigogenin monoacetate followed by hydrolysis (EtOH–KOH). Oxidation by CrO_3 in AcOH and subsequent hydrolysis converts the acetate of (IV) into (III). R. S. C.

Sterols. CXVIII. Action of selenious acid on Δ^5-pregnenediol and on Δ^5-androstenediol. R. E. Marker, H. M. Crooks, jun., and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1941, **63**, 777—779).—Δ^5-Pregnene-3(β) : 20(α)-diol (prep. from $\Delta^{5:16}$-pregnadien-3(β)-ol-20-one by Na–EtOH), m.p. 174—176°, gives a *diacetate*, m.p. 144—146°, which with SeO_2 and NaOAc in boiling C_6H_6–AcOH gives a product, hydrolysed to Δ^5-*pregnene*-3 : 4 : 20-*triol*, m.p. 207—210° (*triacetate*, m.p. 153—154°). With boiling conc. HCl–EtOH this gives Δ^4-*pregnen*-20(α)-*ol*-3-*one*, m.p. 158—160° (*acetate*, m.p. 138—140°), whence CrO_3 in AcOH at room temp. gives progesterone. Δ^5-Androstene-3 : 17-diol diacetate, SeO_2, and NaOAc in C_6H_6–AcOH give similarly Δ^5-*androstene*-3 : 4 : 17-*triol*, m.p. 258—261° (*triacetate*, m.p. 155—156°), and thence by HCl–AcOH testosterone, which is isolated as semicarbazone, m.p. 225° (decomp.), and regenerated therefrom by $H_2C_2O_4$ in 75% EtOH. R. S. C.

III.—TERPENES.

Solvent effects in addition reactions. II. Addition of hydrogen bromide and chloride to α-pinene. G. F. Hennion and C. F. Irwin (*J. Amer. Chem. Soc.*, 1941, **63**, 860—862).—As indicated previously (A., 1939, I, 476), co-ordination between HHal and the solvent greatly decreases the rate of reaction of the acid. Relative reaction rates for α-pinene and HBr are $CHCl_3$ > xylene > C_7H_{16} > $PhNO_2$ > dioxan > $EtOBu^{\alpha}$ > Et_2O and for HCl are $CHCl_3$ > xylene > $PhNO_2$ ≫ MeOH > dioxan > $EtOBu^{\alpha}$ > Et_2O. R. S. C.

Condensation of amino-acids with terpenes. I. Glycine and limonene nitrosochloride. C. F. Krewson (*J. Amer. Pharm. Assoc.*, 1941, **30**, 47—49).—Glycine (1 mol.) and limonene nitrosochloride (1 mol.) in 85% EtOH, heated at 50° for several hr., and then steam-distilled, yield a volatile oil containing carvone, carvoxime, and various unidentified fractions; the residue yielded 3·1% (calc. on glycine used) of *limonenenitrolaminoacetic acid hydrochloride* [*N*-(2-keto-1-$\Delta^{8(9)}$-*p*-menthenyl)glycine oxime hydrochloride], m.p. 141·0—141·5° (uncorr.) (*Cu* derivative, $Cu[C_{10}H_{15}(N{\cdot}OH){\cdot}NH{\cdot}CH_2{\cdot}CO_2]_2{\cdot}CuCl_2$). The mechanism of the formation of the reaction products is discussed.

F. O. H.

***iso*Fenchone. Hydroxymethylene*iso*fenchone and its derivatives.** A. K. Rushentzeva and N. K. Kedrova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 95—97).—*iso*Fenchone with Na and $HCO_2C_5H_{11}$ in Et_2O, followed by H_2O, yields *hydroxymethylene*i*sofenchone* (I), m.p. 103—104° [*Bz*, m.p. 81—82°, and *phenylpyrazole* derivative ($NHPh{\cdot}NH_2$), m.p. 60—61°; *anilide*, m.p. 101—102°], which contains 99% of the enol (Meyer's Br method) after keeping for 6 months. (I) is oxidised (CrO_3 in AcOH) to *iso*fenchocamphoric acid.

A. Lt.

Triterpene group. VIII. Minor triterpenoid constituents of *Manila elemi* resin (continued). (Miss) I. M. Morice and J. C. E. Simpson (*J.C.S.*, 1941, 181—184).—By adsorption on Al_2O_3, *ψ-taraxastanediol* (I), $C_{30}H_{52}O_2$, m.p. 270—272°, $[\alpha]_D^{23}$ −10·9° (*monoacetate*, m.p. 281—284°, $[\alpha]_D^{23}$ −1·5°), has been isolated from the resin; it is the precursor of *ψ*-taraxasterol. (I) is a saturated dihydric alcohol containing C·OH, and it is converted (HCO_2H) by dehydration into *ψ*-taraxasteryl acetate, which with BzO_2H gives the *oxide*, m.p. 265—267°, a reaction not shown by the acetate of (I). From the resin were isolated small amounts of *diol A*, $C_{30}H_{48}O_2$ (?), m.p. 234—236°, $[\alpha]_D^{22}$ −70°±10° (*diacetate*, m.p. 211—212°, $[\alpha]_D^{19}$ +35°), and *alcohol B*, $C_{30}H_{54}O_2$ (?), m.p. 252—254°, $[\alpha]_D^{19}$ −17° (*monoacetate*, m.p. 227—229°, $[\alpha]_D^{23}$ −39°). All [α] in $CHCl_3$. F. R. S.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Action of ultra-violet light on lignin. L. V. Forman (*Paper Trade J.*, 1940, **111**, *TAPPI Sect.*, 266—272).—Lignin (I) in the form of solvent-extracted sprucewood meal undergoes

drastic colour change when irradiated with ultra-violet light, and its OMe content is decreased. The effect of "native" (I), though appreciable, is not so great. Extraction of irradiated (I) with EtOH removes a no. of degradation products) among them being vanillin (II) and a product (OMe 10·6%, similar to native (I). Filter-paper impregnated with an EtOH solution of (II) discolours very rapidly when exposed to ultra-violet light; dehydrodivanillin is probably formed.
H. A. H.

V.—HETEROCYCLIC.

2-Cyanoacetylcoumarone-5-sulphonyl chloride.—See B., 1941, II, 104.

Cannabis indica. **VII. Relation between chemical constitution and hashish activity.** P. B. Russell, A. R. Todd, S. Wilkinson, A. D. Macdonald, and G. Woolfe (*J.C.S.*, 1941, 169—172).—The following compounds prepared from the corresponding coumarin and MgMeI have been tested pharmacologically: 5″-*hydroxy*-2 : 2 : 5′-*trimethyl*-4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzopyran*, b.p. 150—160°/10^{-3} mm. (*acetate*, b.p. 150°/10^{-3} mm.) [from 6-*hydroxy*-5′-*methyl*-7-n-*amyl*-3 : 4-cyclo*hexenocoumarin*, m.p. 188° (*acetate*, m.p. 119—120°)], and the 6″-*hydroxy*-2 : 2-*dimethyl* compound, b.p. 158—165°/10^{-3} mm. [from 5-*hydroxy*-7-n-*amyl*-3 : 4-cyclo*hexenocoumarin*, m.p. 180° (*acetate*, m.p. 80°)]; 5-*hydroxy*-2 : 2 : 4 : 7-*tetramethyl*-Δ^3-*chromen*, m.p. 97° (not tested); 5-*hydroxy*-2 : 2 : 4-*trimethyl*-7-n-*amyl*-Δ^3-*chromen*, b.p. 140—150°/10^{-1} mm. [from 5-*hydroxy*-4-*methyl*-7-n-*amylcoumarin*, m.p. 185° (*acetate*, m.p. 97°)]; 5-*hydroxy*-2 : 2 : 7-*trimethyl*-, b.p. 140—150°/10^{-1} mm. [from 5-*hydroxy*-7-*methyl*-3 : 4-cyclo*pentenocoumarin*, m.p. 254° (*acetate*, m.p. 131°)], and 5-*hydroxy*-2 : 2-*dimethyl*-7-n-*amyl*-3 : 4-cyclo*penteno*-Δ^3-*chromen*, m.p. 78° [from 5-*hydroxy*-7-n-*amyl*-3 : 4-cyclo*pentenocoumarin*, m.p. 176° (*acetate*, m.p. 65—66°)]. The question of chemical constitution and hashish activity is discussed. All b.p. are at bath temp.
F. R. S.

Constitution of natural tannins. VII. Colouring matters derived from β-naphthaldehyde. A. Russell and J. C. Speck (*J. Amer. Chem. Soc.*, 1941, **63**, 851—852; cf. A., 1939, II, 557).—2-$C_{10}H_7$·CHO and the appropriate COPhMe derivative in AcOH give 2-*phenyl*-, decomp. 118°, 2-o-*anisoxy*-, decomp. 110°, 2-2′ : 4′-*di*-, decomp. 132°, and 2-2′ : 3′ : 4′-*tri*-*methoxyphenyl*-1-α-*naphthopyrylium chloride* (I), decomp. 121°. 2-o- and 2-p-*Hydroxy*- and 2-2′ : 4′-*dihydroxy*-*phenyl*-1-α-*naphthopyrylium chloride* (all decomp. ~200°) are obtained as benzoates and liberated therefrom by boiling conc. HCl–EtOH. Hydrolysis of (I) by $AlCl_3$ in boiling PhCl gives the $(OH)_3$-compound, decomp. ~200°.
R. S. C.

Dismutation of some disulphides. IV. F. S. Fowkes and E. W. McClelland (*J.C.S.*, 1941, 187—190).—5 : 5′-Dichloro-2 : 2′-dithiobenzoic acid (I) with Ac_2O and KOAc (130°; 4 hr.) gives 5-*chloro*-3-*acetoxy*-1-*thionaphthen*, m.p. 67°; the Cl in the *p*-position to S thus decreases the tendency of a 2 : 2′-dithiobenzoic acid to undergo dismutation. CH_2Ac_2 and (I) in H_2SO_4 afford 5-*chloro*-3-*hydroxy*-2-*acetyl*-1-*thionaphthen* (II), m.p. 166° (*Ac* derivative, m.p. 132°); 3-*acetoxy*-2-*acetyl*-1-*thionaphthen* has m.p. 127°. NHPh·NH_2 and (II) yield the *hydrazone*, m.p. 162°, which with conc. H_2SO_4 is converted into 8-*chloro*-1-*phenyl*-3-*methyl*-4 : 5-*thionaphthenopyrazole*, m.p. 135°; (II) and H_2O_2–AcOH give 5-*chloro*-3-*hydroxy*-2-*acetyl*-1-*thionaphthen* 1 : 1-*dioxide*, m.p. 265°. 5-Chloro-3-hydroxy-1-thionaphthen and NHPh·NH_2 afford 10-*chlorothionaphthindole*, m.p. 222°. The 3-Ac derivative with H_2O_2–AcOH yields 5-*chloro*-3-*acetoxy*-1-*thionaphthen* 1 : 1-*dioxide*, m.p. 164°, under mild conditions, but under more vigorous conditions it gives the 3-*hydroxy*-*dioxide*, m.p. 194°, the *phenylhydrazone*, m.p. 290—292°, of which could not be indolised. Thus the Cl substitution of hydroxythionaphthens has no marked effect on their reactivity. 2 : 2′-Dithiobenzoic acid undergoes dismutation in neutral media.
F. R. S.

α-Coumarilyl- and α-thionaphthenoyl-acetates etc.—See B., 1941, II, 109, 132.

Condensation of 6-amino-2-hydroxypyridine with *p*-acetamidobenzenesulphonyl chloride. M. A. Phillips (*J.C.S.*, 1941, 291—293).—6-Amino-2-hydroxypyridine sulphate in C_5H_5N with one equiv. of *p*-NHAc·C_6H_4·SO_2Cl gives mainly 6-*amino*-2-*pyridyl* p-*acetamidobenzenesulphonate* (I) and some 6-p-*acetamidobenzenesulphonamido*-2-*pyridyl* p-*acetamidobenzenesulphonate* (II), m.p. 222°. Hydrolysis (HCl) of (I) yields 6-*amino*-2-*pyridyl* p-*aminobenzenesulphonate*, m.p. 148°, and treatment with NaOH affords 6-amino-2-hydroxypyridine. Further treatment of (I) with *p*-NHAc·C_6H_4·SO_2Cl leads to (II), which with NaOH gives 6-*hydroxy*-2-(p-*aminobenzenesulphonamido*)*pyridine*, m.p. 239—240°.
F. R. S.

Piperidine derivatives.—See B., 1941, III, 80.

Chromic acid oxidation of quinoline homologues. Oxidation of *Bz*-ethylquinolines to quinolyl methyl ketones. R. A. Glenn and J. R. Bailey [with, in part, W. N. Axe] (*J. Amer. Chem. Soc.*, 1941, **63**, 641—643).—Oxidation of 8-alkylquinolines by $K_2Cr_2O_7$ is more rapid than that by CrO_3, owing to catalysis (proved experimentally) of the latter reaction by $KHSO_4$. Max. yields of acid are obtained by using < theoretical amount of oxidant. The following yields of 8-carboxylic acid and 8-Ac derivative, respectively, are obtained by (*a*) CrO_3–$KHSO_4$–H_2SO_4 and (*b*) $K_2Cr_2O_7$–H_2SO_4 from the bases named: 2 : 3 : 8-trimethyl- (*a*) 85, 0, 2 : 3-dimethyl-8-ethyl- (*a*) 56, 12, (*b*) 50, 0, 2 : 4-dimethyl-8-ethyl- (*a*) 0, 36, (*b*) 30, 0, 2 : 3-dimethyl-8-*n*-propyl- (*a*) 83, 0, 2 : 3 : 4 : 8-tetramethyl- (*a*) 86, 0, 8-ethyl- (*b*) 40, 40, 2-methyl-8- or -6-ethyl- (*b*) 0, 75, 3-methyl-8-ethyl- (*b*) 0, 80, 2 : 4-dimethyl-6-ethyl- (I) (*b*) 0, 30, 2 : 3 : 4-trimethyl-8-ethyl- (*b*) 25, 50, 3-methyl-2 : 8-diethyl- (II) (*b*) 10, 55, and 3-methyl-2 : 6-diethyl-quinoline (III) (*b*) 0, 85%. The following are described: *semicarbazones* of 2-methyl-6-, m.p. 262°, 3-methyl-8-, m.p. 226—227°, 2 : 3-dimethyl-8-, m.p. (+H_2O) 239°, 2 : 4-dimethyl-6-, m.p. (+2H_2O) 251°, 2 : 4-dimethyl-6-, m.p. (+2H_2O) 262°, 2 : 3 : 4-trimethyl-8-, m.p. (+2H_2O) 258—259°, 3-methyl-2-ethyl-8-, m.p. 243°, and 3-methyl-2-ethyl-6-, m.p. 251°, -acetylquinoline; 3-methyl-2-ethylquinoline-8-carboxylic acid, new m.p. 223°; (I) (from boiling *p*-C_6H_4Et·NH_2 and CH_2Ac_2 and, later, H_2SO_4 at 100°), b.p. 299—300°/742 mm. (*picrate*, m.p. 190—191°); (II) (from *o*-C_6H_4Et·NH_2 and EtCHO), m.p. 18·5—19·5°, b.p. 298°/754 mm. (*picrate*, m.p. 194—195°); (III), b.p. 313·5°/748 mm. (*picrate*, m.p. 152—153°).
R. S. C.

Nitrogen compounds in petroleum distillates. XIX. Isolation from Californian petroleum, and synthesis, of 2 : 3 : 8-trimethyl-4-ethylquinoline. XX. Isolation of 2-methyl-8-ethylquinoline from Californian petroleum; proof of its structure by degradation and synthesis. R. A. Glenn and J. R. Bailey (*J. Amer. Chem. Soc.*, 1941, **63**, 637—638, 639—641; cf. A., 1940, II, 357).—XIX. The fraction, b.p. 308—313°, of the bases previously (A., 1939, II, 24) obtained from Californian petroleum yields, by countercurrent extraction, 2 : 3 : 4-trimethyl-8-ethyl-, 2 : 3 : 4 : 8-tetramethyl-, and 2 : 3 : 8-*trimethyl*-4-*ethyl*-*quinoline* (I), b.p. 310—311°/748 mm. [*picrate*, m.p. 178°; *nitrate*, m.p. 161° (decomp.); *phthalone*, m.p. 158° (red Na salt)]. $K_2Cr_2O_7$–H_2SO_4 oxidises (I) to 2 : 3-*dimethyl*-4-*ethylquinoline*-8-*carboxylic acid*, m.p. 178°, converted by distillation with soda–lime into 2 : 3-*dimethyl*-8-*ethylquinoline* (II), b.p. 302°/749 mm. (*picrate*, m.p. 220—221°). Condensation of $COEt_2$ and paraldehyde by dry HCl at 0° and subsequent interaction with NH_2Ph or *o*-C_6H_4Me·NH_2 and conc. HCl at 100° gives (II) and (I), respectively. (I) is the first base isolated from petroleum to contain in the *Py*-nucleus an alkyl other than Me.

XX. The fraction, b.p. 258—264°, of the bases obtained as above yields by distillation and crystallising the picrates 2-*methyl*-8-*ethylquinoline* (III), b.p. 263·0—263·5°/755 mm. [*picrate*, m.p. 169°; *phthalone*, m.p. 246° (red Na salt); *nitrate*, m.p. 143° (decomp.)], and a base, $C_{12}H_{13}N$ (*picrate*, m.p. 153·0—153·5°). SeO_2 converts (III) in boiling EtOH into 8-ethylquinoline-2-aldehyde (*semicarbazone*, m.p. 189—190°), oxidised by H_2O_2–$COMe_2$ (90%) or Ag_2O–EtOH (8% yield) to 8-*ethylquinoline*-2-*carboxylic acid*, m.p. 121°, which, when fused alone, gives 8-*ethylquinoline* (IV), b.p. 256° [*picrate*, m.p. 146° (decomp.); *nitrate*, m.p. 146°], also obtained with some quinoline from *o*-C_6H_4Et·NH_2, $PhNO_2$, $FeSO_4$, H_3BO_3, glycerol, and H_2SO_4. *o*-C_6H_4Et·NH_2, MeCHO, $ZnCl_2$, and HCl give 22% of (III). $K_2Cr_2O_7$–H_2SO_4 oxidises (III) to 8-acetyl-2-methylquinoline (46%) [*picrate*, m.p. 182° (decomp.); *semicarbazone*, m.p. 209°], stable to $K_2Cr_2O_7$ but oxidised by NaOBr to 2-methylquinoline-8-carboxylic acid. $K_2Cr_2O_7$–H_2SO_4 oxidises (IV) to 8-acetylquinoline (40%) (semicarbazone, new m.p. 225°) and quinoline-8-carboxylic acid (40%).
R. S. C.

Quinoline "sulphanilamides."—See B., 1941, III, 109.

Synthesis of analgesics. P. V. A. Raman (*J. Indian Chem. Soc.*, 1940, **17**, 715—720).—Homopiperonylamine (**I**) is condensed with Et furoate at 100° and the crude amide is cyclised with $POCl_3$ in boiling PhMe to 6 : 7-*methylenedioxy*-1-2′-*furyl*-3 : 4-*dihydroisoquinoline*, m.p. 95—96° [*picrate*, m.p. 206° (decomp.); *methiodide* (**II**), m.p. 238° (decomp.)]. (**II**) is reduced by Zn dust and dil. H_2SO_4 at 100° to 6 : 7-methylenedioxy-1-2′-furyl-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, isolated as the *picrate*, m.p. 100° (decomp.). *Me* 7-*methoxycoumarone*-2-*carboxylate*, m.p. 79°, and (**I**) at 100° afford 7-*methoxy*-2-*coumaronylhomopiperonylamide*, m.p. 86°, cyclised ($POCl_3$ in boiling PhMe) to 6 : 7-*methylenedioxy*-1-7′-*methoxy*-2′-*coumaronyl*-3 : 4-*dihydroisoquinoline*, m.p. 140—142° [*picrate*, m.p. 220° (decomp.); *methiodide* (**III**), m.p. 190—191° (decomp.)]. Reduction (Zn dust and dil. H_2SO_4) of (**III**) gives 6 : 7-methylenedioxy-1-7′-methoxy-2′-coumaronyl-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, an oil, isolated as the *picrate*, m.p. 185—187° (decomp.). 9-Phenanthroyl chloride and (**I**) in conc. KOH yield the non-cryst. 6 : 7-methylenedioxy-1-9′-phenanthryl-3 : 4-dihydro*iso*quinoline [*picrate*, m.p. 145—147° (decomp.)]; the corresponding methiodide is reduced to the non-cryst. 6 : 7-methylenedioxy-1-9′-phenanthryl-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, isolated as the *picrate*, m.p. 105—108° (decomp.). Et β-2-furylpropionate and (**I**) at 100° afford β-2-*furylpropionylhomopiperonylamide*, m.p. 92°, and (**I**) and Et β-2-5′-phenylfurylpropionate give β-2-5′-*phenylfurylpropionylhomopiperonylamide*, m.p. 104·5°, neither of which could be satisfactorily cyclised. H. W.

Amino-alcohols derived from carbazole. II. L. Ruberg and L. Small (*J. Amer. Chem. Soc.*, 1941, **63**, 736—741; cf. A., 1938, II, 380).—3-Acetyl-9-methylcarbazole, paraldehyde, and the appropriate *sec.* amine in boiling abs. EtOH–N_2 give 3-ω-*dimethylamino*-, m.p. 72·5—73° (*hydrochloride*, m.p. 193·5—194·5°), 3-ω-tetrahydroquinolino-, an oil (*hydrochloride*, sinters at 198·5°, m.p. 201—202°; *picrate*, sinters at ~170°, m.p. 177·5—178·5°), and 3-ω-diethylamino-propionyl-9-methylcarbazole, an oil (*hydrochloride*, sinters at ~162°, m.p. 167—168·5°; *picrate*, sinters at ~134°, m.p. 143—143·5°), the hydrochlorides of which with H_2–PtO_2 in MeOH give 9-*methyl*-3-γ-*hydroxy*-α-*dimethylamino*-, m.p. 122·5—123° [*picrate*, sinters at >145°, m.p. 157·5—158·5° (gas)], -γ-tetrahydroquinolino-, amorphous [*hydrochloride*, sinters at >177°, m.p. 187° (gas)], and -γ-diethylamino-propylcarbazole [*hydrochloride* (**I**), sinters at >129°, m.p. 132—134°]. Conversion of (**I**) into the oily base and treatment thereof with HCl–EtOH–Et_2O gives a *hydrochloride*, $C_{20}H_{25}N_2Cl$, sinters at ~184°, m.p. 189—190·5°. 9-Acetylcarbazole, $CH_2Cl{\cdot}COCl$, and $AlCl_3$ in CS_2 give 94% (cf. lit.) of the 2-$CH_2Cl{\cdot}CO$ derivative, sinters at 178°, m.p. 181—183°, hydrolysed by 20% aq. H_2SO_4 in boiling EtOH to 2-chloroacetylcarbazole (**II**), m.p. 208—210°, the structure of which is proved by fusion with KOH to give the 2-carboxylic acid. With Me_2SO_4–KOH, (**II**) gives 2-*chloroacetyl*-9-*methylcarbazole*, m.p. 173·5—175°. With $NHEt_2$ in C_6H_6 at 100° (tube), (**II**) gives 2-ω-*dimethylaminoacetylcarbazole*, m.p. 134—136° (decomp.; sinters at >126°; air), 155·5—156·5° (no decomp.; sinters at >150°; vac.) [*hydrochloride*, +0·5H_2O, m.p. 190·5—193° (decomp.; sinters at >100°); *picrate*, m.p. 164—165° (sinters at 160°)], reduced as hydrochloride by H_2–PtO_2–60% EtOH or, better, 5% Na–Hg in HCl–aq. EtOH to 2-α-*hydroxy*-β-*diethylaminoethylcarbazole*, m.p. 151—152° [*hydrochloride*, m.p. 182·5—184°; *styphnate*, sinters at >174°, m.p. 179—180° (decomp.); N-*oxide*, sinters at >176°, m.p. 181° (gas)]. R. S. C.

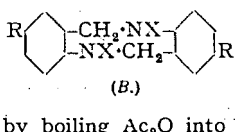
Retene field. XI. Synthesis of retopyridines (naphthaquinolines) from 3-aminoretene. (Miss) S. A. Cassaday and M. T. Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 703—708; cf. A., 1939, II, 206).—γ-Keto-γ-3-retyl-*n*-butyric acid (modified prep.) gives an *oxime*, m.p. 165—166°, and an *Et* ester, m.p. 92·5—93°, the *oxime*, m.p. 105—106°, of which with PCl_5 in Et_2O gives *Et* 3-*retylsuccinamate*, m.p. 168—169°, and thence (KOH–Pr$^{\alpha}$OH or HCl–AcOH–H_2O) 3-aminoretene (**I**) (11 g. from 100 g. of retene) [*hydrochloride*, m.p. 267—273° (vac.); Ac derivative, new m.p. 240—241°], the less advantageous prep. of which from 3-acetylretene is modified. With $PhNO_2$, glycerol, $FeSO_4$, and H_2SO_4 at 140—145° and later 160—170°, (**I**) gives 7-*methyl*-3-*isopropylnaphtha*[2 : 1-g]*quinoline* [6′-*methyl*-6-*isopropylnaphtha*-1 : 2-7′ : 6′-*quinoline*] or 6-*methyl*-10-*isopropylnaphtha*[1 : 2-f]-*quinoline* [7′-*methyl*-6-*isopropylnaphtha*-1 : 2-5′ : 6′-*quinoline*], m.p. 87·5—88·5° [*picrate*, m.p. 277—279° (decomp.); *hydrochloride*, +3H_2O (tenaciously held), m.p. 96—101°], which resists reduction. With paraldehyde in conc. HCl at 100°, (**I**) gives 7 : 10-*dimethyl*-3-*isopropylnaphtha*[2 : 1-g]- or 3 : 6-*dimethyl*-10-*isopropylnaphtha*[1 : 2-f]-*quinoline*, m.p. 110—111° [*hydrochloride*, +3H_2O (tenaciously held), m.p. 258—261°; *picrate*, m.p. 221—226° (decomp.)]. With PhCHO and $AcCO_2H$ in boiling EtOH, (**I**) gives 5-*keto*-4-3′-*retylimino*-2-*phenyl*-1-3′-*retylpyrrolidine*, m.p. 218—219° [*picrate*, m.p. 234·5—235·5° (decomp.)], which with NH_2OH,HCl and $BaCO_3$ in boiling MeOH gives 5-*keto*-4-*oximino*-2-*phenyl*-1-3′-*retylpyrrolidine*, m.p. 208—209°. With PhCHO in boiling EtOH, (**I**) gives the *CHPh*: derivative, m.p. 88—89°. M.p. are corr. R. S. C.

Barbituric acids.—See B., 1941, III, 108.

Direct synthesis of 1 : 2 : 4 : 5-tetra-substituted iminazoles. F. Lions and E. Ritchie (*J. Proc. Roy. Soc. N. S. Wales*, 1940, **74**, 365—372).—OH·CHMe·NH_2, Ac_2, and NH_2Me in EtOH at room temp. give 1 : 2 : 4 : 5-*tetramethylglyoxaline*, m.p. 58° (*picrate*, m.p. 189°). A similar interaction of the respective α-diketone, primary amine, and aldehyde-ammonia affords: 1-n-*butyl*-, b.p. 145—146°/28 mm. (*picrate*, m.p. 145°), 1-*phenyl*-, b.p. 170—174°/29 mm. (*picrate*, m.p. 122°), 1-p-*tolyl*-, b.p. 176—180°/20 mm. (*picrate*, m.p. 123°), 1-(β-*phenylethyl*)-, b.p. 209—212°/28 mm. (*picrate*, m.p. 164°), and 1-*benzyl*-2 : 4 : 5-*trimethylglyoxaline*, m.p. 81° (*picrate*, m.p. 127°); 1-*benzyl*-2-*methyl*-4 : 5 : 6 : 7-*tetrahydrobenziminazole*, m.p. 76° (*picrate*, m.p. 143°), and 2-methyl-4 : 5 : 6 : 7-tetrahydrobenziminazole, m.p. 220° (picrate, m.p. 184°) (cf. Hartmann *et al.*, A., 1939, II, 37); 1-*benzyl*-2-n-*propyl*-4 : 5-*dimethylglyoxaline*, b.p. 194—196°/19 mm. A. T. P.

Pyrazolone derivatives.—See B., 1941, II, 172.

Analogues of Troeger's base and related compounds. T. R. Miller and E. C. Wagner (*J. Amer. Chem. Soc.*, 1941, **63**, 832—836).—*p*-$C_6H_4R{\cdot}NH_2$, (*p*-$C_6H_4R{\cdot}NH)_2CH_2$, (*p*-$C_6H_4R{\cdot}N{\cdot}CH_2)_3$ (R = OMe or OEt), 6-methoxy-3-*p*-anisyl- or 6-ethoxy-3-*p*-phenetyl-1 : 2 : 3 : 4-tetrahydroquinazoline with 39% CH_2O or conc. HCl at room temp. give the Troeger bases (*A*), 6-*methoxy*-3-p-*anisyl*-, m.p. 172—172·5° (corr.) [*hydrochloride*, +2H_2O, m.p. 115—120°, and anhyd., m.p. 213—215°; picrate, m.p. 207·5—208·5° (corr.)], and 6-*ethoxy*-3-p-*phenetyl*-1 : 2′-*methylene*-1 : 2 : 3 : 4-*tetrahydroquinazoline*, m.p. 131·5—132° (corr.) [*hydrochloride*, +2H_2O, m.p. 135—137°, and anhyd. m.p. 236—240° (corr.); picrate, m.p. 196·5—197·5°], converted by aq. HNO_2 into *nitrosoamines* (*B*) [X = NO; R = OMe, m.p. 207·5—208·5° (decomp.), and OEt, m.p. 184—186° (corr.)], and by boiling Ac_2O into CH_2O and *compounds* (*B*) [X = Ac; R = OMe, m.p. 298—300° (decomp.), and OEt, m.p. 232·5—233·5° (corr.)], respectively. However, *p*-$C_6H_4R{\cdot}NH_2$, (*p*-$C_6H_4R{\cdot}NH)_2CH_2$, (*p*-$C_6H_4R{\cdot}N{\cdot}CH_2)_3$, 2 : 5 : 1-$NH_2{\cdot}C_6H_3R{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4R$-*p* (R = Cl or Br), or the derived tetrahydroquinazoline gives 6-*chloro*-3-p-*chlorophenyl*- (**I**), m.p. 135—136° [*hydrochloride*, m.p. 273—274° (decomp.); picrate, m.p. 188—189° (corr.); *phenylurethane*, m.p. 141—142° (corr.)], and 6-*bromo*-3-p-*bromophenyl*- (**II**), m.p. 139·5—140·5° [*hydrochloride*, m.p. 276—278° (decomp.); *picrate*, m.p. 203·5—204·5° (corr.); *phenylurethane*, m.p. 159·5—160·5° (corr.)], -1-*hydroxymethyl*-1 : 2 : 3 : 4-*tetrahydroquinazoline*, whence red P and boiling 57% HI yield >1 mol. of *p*-$C_6H_4Hal{\cdot}NH_2$. (**I**) and (**II**) are considered to be intermediates in the formation of (*A*) (cf. A., 1935, 1118), although attempts to achieve this conversion failed. In two experiments a substance, m.p. 121°, was obtained instead of (**IV**). R. S. C.



(*B.*)

Adamkiewicz, Hopkins and Cole, and Rosenheim tests for tryptophan. Investigation of the configuration of the organic molecule responsible for the colour formation and its bearing on the constitution of yohimbine; action of formaldehyde on tryptophan. D. G. Harvey, E. J. Miller, and W. Robson (*J.C.S.*, 1941, 153—159).—If to an aq. solution of 2 : 3 : 4 : 5-tetrahydro-β-carboline-4-carboxylic acid (**I**), conc. H_2SO_4 containing a trace of an oxidising agent is added so that the two liquids do not mix, the play of colours at their zone of contact resembles that obtained when tryptophan (**II**) is subjected to the modified Adamkiewicz procedure. Hence (**I**) may be used to test conc. H_2SO_4 for the presence of oxidising agents. The colour reaction has been carried out with several compounds and only those possessing the struc-

ture of (I) give it. The following have been prepared: *Me 2-methyl-2 : 3 : 4 : 5-tetrahydro-β-carboline-4-carboxylate hydrochloride*, m.p. 264° (decomp.), *2-hydroxymethyl-*, m.p. 234°, *3-methyl-* (+H_2O), m.p. 208°, *2 : 3-dimethyl-*, m.p. 243—245°, and *2-phenyl-3-methyl-2 : 3 : 4 : 5-tetrahydro-β-carboline-4-carboxylic acid* (+H_2O), m.p. 219°, and *2 : 3 : 4 : 5-tetrahydro-β-carboline-2 : 4-dicarboxylic acid*, m.p. ~270° (decomp.). The reaction with (II) involves the formation of (I) or a derivative thereof and then oxidation to the blue pigment. Yohimbine (III) behaves like (I) towards conc. H_2SO_4 containing an oxidising agent. Therefore probably the CO_2Me in (III) is at $C_{(5)}$ and not at $C_{(10)}$ as postulated by Hahn *et al.* (A., 1934, 667). F. R. S.

Fluorescence of purines and pyrimidines.—See A., 1941, I, 193.

Cu and Co tetra-(4)-pyridylphthalocyanines.—See B., 1941, II, 77.

αβ-Unsaturated amino-ketones. IV. Mechanism of the reaction of α-bromo-αβ-unsaturated ketones with *sec.* amines. N. H. Cromwell (*J. Amer. Chem. Soc.*, 1941, **63**, 837—839; cf. A., 1941, II, 110).—The mechanism previously proposed for the reaction of CHR:CBr·COR′ with NHR_2 is confirmed, but the course of the reaction is partly dependent on the nature of the base. α-Bromo-α-piperidino-β-phenylpropiophenone (1 mol.) and morpholine (2 mols.) in boiling EtOH give *α-piperidino-β-morpholino-β-phenylpropiophenone* (I), *forms*, m.p. 174—175° and 155—157°, and CHPh:C(NC_5H_{10})·COPh (II), m.p. 102—103°. Hydrolysis of (I) by 15% H_2SO_4 gives ω-piperidinoacetophenone (*hydrochloride*, m.p. 226—227°), PhCHO, and morpholine (not isolated). In boiling EtOH (I) does not yield (II) and the two products thus arise by independent reactions. Piperidine and α-bromo-α-morpholino-β-phenylpropiophenone in boiling EtOH give mixtures (*a*) CHPh:CR·COPh (acid hydrolysis gives 80—85% of COPh·CO·CH_2Ph), and (*b*) NC_5H_{10}·CHPh·CHR·COPh (hydrolysis gives mixed CH_2R·COPh), in which R = piperidino and morpholino. R. S. C.

Thiazole "sulphanilamides."—See B., 1941, III, 133.

Cyanine dyes.—See B., 1941, II, 110, 140, 170.

Gelsemine. II. Bromination and nitration. T. Q. Chou and T. T. Chu (*J. Amer. Chem. Soc.*, 1941, **63**, 827—828; cf. A., 1940, **II**, 360).—Gelsemine and Br in $CHCl_3$ at <0° give *dibromo-*, m.p. 309° (decomp.), converted by dil. aq. Na_2CO_3 into *bromo-gelsemine*, m.p. >320°. Dihydrogelsemine and HNO_3–H_2SO_4 at −7°, later 5°, give *dinitrogelsemine*, m.p. 257—258° (decomp.), $[\alpha]_D^{23}$ +6·6° [*nitrate*, m.p. 219—221° (decomp.), $[\alpha]_D^{22}$ −61·7° in MeOH; *methiodide*, m.p. 255—256°, $[\alpha]_D^{18}$ −68·5° in MeOH]. R. S. C.

Optical activity of quinine and some of its salts in mixtures of water and ethyl alcohol. J. C. Andrews and B. D. Webb (*Ind. Eng. Chem.* [*Anal.*], 1940, **13**, 232—233).—Data are given of the variation in optical activity of quinine, its dihydrochloride and sulphate in various mixtures of H_2O–EtOH, and on the change of rotation as the base is treated with increasing proportions of HCl and H_2SO_4, each in that concn. of aq. EtOH which gives the max. α for each salt. J. D. R.

Alkaloids of Chinese Hanfongchi. III. Hanfongchine *C*. C. F. Hsu (*J. Chinese Chem. Soc.*, 1940, **7**, 123—128).—The aq. NH_3 extract after removal of hanfongchine *A* and *B* when conc. and extracted with hot C_5H_{11}·OH yields *hanfongchine* C, a phenol, $C_{13}H_{10}O_2(OH)_2(OMe)_2NMe,4H_2O$ or $C_{27}H_{23}O_5(OH)_4(OMe)_3(NMe)_2,8H_2O$, m.p. 215—217° (decomp.), $[\alpha]_D^{23}$ −12·9° in H_2O [hydrochloride, m.p. 220—222° (decomp., darkening at 214°); methiodide, m.p. 182—184°; aurichloride, m.p. 118° (decomp., contracting at 90°); platinichloride, m.p. 204° (decomp., darkening at 200°)], which gives a green–dark green colour with $FeCl_3$, and other colour reactions. A. Li.

VI—ORGANO-METALLIC COMPOUNDS.

Preparation of 4-acetamido-2-hydroxyphenylarsenoxide. M. A. Phillips (*J.C.S.*, 1941, 192).—*Biscarboxymethyl 4-acetamido-2-hydroxyphenylthioarsinite*, m.p. 160—161°, obtained from Na thiolacetate and 4 : 2 : 1-NHAc·C_6H_3(OH)·AsO_3H_2, when dissolved in 10% NaOH to a neutral solution and mixed with a neutral solution of *p*-benzarsenious acid, gives 4 : 2 : 1-NHAc·C_6H_3(OH)·AsO in 73% yield. F. R. S.

Sulphophenylarsinic acids and their derivatives. IV. Derivatives of *p*-sulphonamidophenylarsinic acid. J. F. Oneto and E. L. Way (*J. Amer. Chem. Soc.*, 1941, **63**, 762; cf. A., 1940, II, 360).—*p*-AsO_3H_2·C_6H_4·SO_2Cl and the appropriate amine in warm H_2O give p-*arsinobenzenesulphon-dimethylamide*, softens at 166—168°, -anilide, -p′-*carboxyanilide*, and -p′-*sulphonamidoanilide*, converted by HI into the derived *di-iodoarsines*, m.p. 132·5—134°, 125—126°, 234—236°, and 195—197°, respectively. Hydrolysis by aq. NH_3 then gives p-*sulphon-dimethylamido-*, anhyd. and +H_2O, -p′-*carboxyanilido-*, +H_2O, *-anilido-*, and -p′-*sulphonamidoanilido-*, +H_2O, *-phenylarsinoxide*. R. S. C.

Relative reactivities of organo-metallic compounds. XXXV. Colour tests for organo-bismuth and other organo-metallic compounds. H. Gilman and H. L. Yablunky (*J. Amer. Chem. Soc.*, 1941, **63**, 839—844; cf. A., 1940, II, 385).—$BiAr_3Cl_2$ with LiAr or MgArHal in C_6H_6 gives a deep purple colour; if the solution is boiled, cooled, and hydrolysed by H_2O, the org. layer is yellow to orange. Organo-metallic compounds more reactive than MgArHal give only the yellow or orange colour after hydrolysis. Less reactive Mg compounds, other types of Bi compounds, and alkyl compounds give no colour. The sensitivity is approx. that of the Michler's ketone test. Steric hindrance (*e.g.*, mesityl groups) may interfere with the test. Application of the test indicates that in the reaction of carbazole with MgMeI migration of MgI occurs on heating prior to carbonation. R. S. C.

VII.—PROTEINS.

Analysis of proteins. XIII. Caseo-phosphopeptone. J. Lowndes, T. J. R. Macara, and R. H. A. Plimmer (*Biochem. J.*, 1941, **35**, 315—320).—Caseo-phosphopeptone, obtained from caseinogen by Levene and Hill's method (A., 1933, 1062) and purified by repeated pptn. of the Pb salt, is an octapeptide containing N 10·56, P 5·77 (N : P ratio 4 : 1) and glutamic acid 26·8% (2 mols. per mol. of octapeptide) but no S, diamino-acids, tyrosine, tryptophan, or threonine. Of the total N 12·6% is amino-N. All the N is converted into NH_2-N in 48 hr. by treatment with 20% HCl and all P is removed by 5·5N-HCl in 48 hr. at 100° (but not by 0·25N-NaOH at 37° in 48 hr. or more). The acidity and the ratio of acidic H to N atoms indicate that, of 6 replaceable H atoms, two are in H_3PO_4 radicals, two in the glutamic acid residues, one in a terminal CO_2H, and one in another CO_2H. Oxidation with KIO_4 after hydrolysis for 36 hr. with 5·5N-HCl indicates the presence of 2 mols. of serine, hydroxyglutamic acid being probably absent. The results and those of Posternak (A., 1928, 1149) and Damodaran and Ramachandran (A., 1941, II, 115) suggest that the octapeptide is probably constituted thus: phosphoserylglutamic–X–X–phosphoseryl-glutamic–X–X, where X probably represents *iso*leucine (3 mols.) and aspartic acid (1 mol.). W. McC.

Amino-acids of phosphopeptone. C. Rimington (*Biochem. J.*, 1941, **35**, 321—327; cf. A., 1927, 1211).—Re-examination of the material previously obtained suggests that it consists of a nona- ($C_{37}H_{60}O_{33}N_9P_3$) and a deca-peptide ($C_{43}H_{71}O_{34}N_{10}P_3$) which each yield ~4 mols. of dicarboxylic acid per mol. when boiled for 48 hr. with 20% HCl. Hydroxyglutamic acid and threonine are absent but glutamic acid (I) is obtained in low yield. The hydrolysate of the decapeptide yields *iso*leucine (II) and probably contains phosphoserine. At 37°, 1% NaOH removes ~67% of the total P of phosphopeptone as PO_4''', the time-curve of the hydrolysis strongly resembling that for hydrolysis by bone-phosphatase. The decapeptide is possibly formed by the combination of 5 mols. of (I), one mol. of (II), 4 mols. of serine, and 3 H_3PO_4, 12 H_2O being eliminated, and the nonapeptide of the same constituents except (II), 11 H_2O being eliminated. W. McC.

Coupled oxidation of ascorbic acid and hæmoglobin. II. Formation and properties of choleglobin. III. Determination of choleglobin and of hæmoglobin and ascorbic acid consumption. IV. Labile iron of blood: production during choleglobin formation. J. W. Legge and R. Lemberg (*Biochem. J.*, 1941, **35**, 328—338, 339—352, 353—362; cf. A., 1939, III, 650).—II. The prep. of choleglobin (I) and cholehæmochromogen (II) by coupled oxidation of hæmoglobin (from cryst. horse oxyhæmoglobin or washed erythrocytes of sheep, ox, and horse) and ascorbic acid (V) is described. Reduced (I) has an absorption band at 628—630 mμ., increased in strength by

$Na_2S_2O_4$ and by incubation for short periods. After 30 min. incubation the band is replaced by a band at ~670 mμ. due to Fe^{III} choleglobin or oxycholeglobin (III); this change is reversed by $Na_2S_2O_4$. CO causes replacement of the band at 670 mμ. by a band at 628 mμ. due to CO-choleglobin production. CO also reacts with an alkaline solution of (II), shifting the absorption band from 618 to 628 mμ. Alkali converts (I) into denatured globin-cholehæmochromogen and shifts the band to 615—622 mμ. The green insol. pigment (chiefly Fe^{III} cholehæmochromogen) produced by denaturation when coupled oxidation has continued for > ~45 min. shows the absorption band of ferrous (II) at 616—618 mμ. (shifted to 628 mμ. by CO) when reduced with NaOH–$Na_2S_2O_4$. In C_5H_5N, this band is at 619 mμ.; in dil. AcOH and in neutral aq. suspension the band is at 628 mμ. Further oxidation of (I) and (II) occurs when coupled oxidation is continued for several hr., substances having absorption spectra similar to those of verdohæmatin compounds being produced. It is not known whether (I) combines reversibly with O_2 but, if (III) exists, it is more labile than oxyhæmoglobin (IV). Study of the action of H_2O_2 on (IV) in presence of KCN shows that cholehæmatin is distinct from verdohæmatin and that Barkan and Schales' "pseudohæmoglobin" (A., 1938, III, 551) is Fe^{II} denatured globin-cyancholehæmochromogen.

III. A spectrophotometric method of measuring the rate of production of (I) and (II) from hæmoglobin (VI) and methæmoglobin is described. The rate is diminished when AcSH, glutathione, or cysteine replaces (V) but not when reducton replaces it. At first, (I) is the only oxidation product but later other substances in addition to (I) and (II) are produced. At p_H 7·2 and 37° (I) is produced from (VI) in presence of concns. of (V) and glutathione such as occur in the tissues, glutathione increasing the rate of production by more than the val. expected from additive calculation. The reaction velocity is increased, without affecting (V) oxidation, by diminishing O_2 pressure to 15 mm. or by adding inhibitor for Cu [which prevents autoxidation of (V)] and is doubled by changing the p_H from 7·2 to 8·5. The temp. coeff. is high. In air, without shaking, approx. 10 mols. of (V) are oxidised per mol. of (I) produced. (VI) in erythrocytes is protected from rapid oxidation by the low permeability of the cell membrane and by an inhibitor in the stromata. H_2O_2 produces (I) from (VI) even in the absence of reducing substances. The first step in the production is probably transfer of H from (V) to (IV), a Fe^{II} (VI)–H_2O_2 compound being produced. This compound is converted partly into (I) and partly into methæmoglobin.

IV. Of the labile Fe of blood and (VI) solutions, 67% is probably an artefact arising from the oxidation of the prosthetic group of (VI) by the O_2 produced from (IV) by acid. The fraction of the labile Fe split off even in presence of CO is at least partly derived from a bile pigment–(VI) which yields bile acids when treated with acid, a small part only being derived from blood-catalase. The increase in the proportion of labile Fe which occurs during coupled oxidation of (VI) and (V) ∝ the concn. of (I) produced. Incubation of (I) for 16 hr. with 0·1N-HCl liberates ~66% of the Fe, the remainder being found as cholehæmatin in the ppt. of denatured protein. The elimination of Fe from (I) by acid is apparently not inhibited by CO or reducing substances. W. McC.

Some applications of periodic acid to the study of the hydroxyamino-acids of protein hydrolysates. I. Liberation of acetaldehyde and higher aldehydes by periodic acid. II. Detection and isolation of formaldehyde by periodic acid. III. Ammonia split from hydroxyamino-acids by periodic acid. IV. Hydroxyamino-acid fraction of wool. V. "Hydroxylysine." A. J. P. Martin and R. L. M. Synge (*Biochem. J.*, 1941, **35**, 294—314; cf. A., 1940, II, 385).—I. *dl*-Threonine (I) and HIO_4 at room temp. give a max. yield of ~70% of MeCHO (removed by aëration and absorbed in aq. $NaHSO_3$) at p_H ~7 in aq. $NaHCO_3$, independently of the presence of other amino-acids. *dl*-Serine (II) and -alanine, and *l*-cystine, -methionine, -tyrosine, etc., afford no MeCHO. Protein hydrolysates are examined. Volatile aldehydes from wool, casein, and gelatin are converted into the 2 : 4-dinitrophenylhydrazone; MeCHO only is identified. In the case of wheat gluten a little EtCHO is possibly obtained also, but this is not certain, as previous results are unreliable owing to possible confusion arising from the dimorphism of the 2 : 4-dinitrophenylhydrazone of MeCHO. *X*-Ray powder photographs [Miss F. O. Bell] failed to establish with certainty the presence of any derivative other than from MeCHO. A micro-method for the separation of 5% of EtCHO in a mixture with MeCHO, depending on "carrier" distillation using Et_2O as a solvent, is described.

II. No satisfactory method is found for the determination of CH_2O resulting from the action of HIO_4 on serine etc. Conditions for pptn. of CH_2O by dimedon are studied; the presence of other amino-acids seriously lowers the yield.

III. (I) or (II) and HIO_4 in 50% aq. K_2CO_3 at room temp. yield 88% or 83% of 1 mol. of NH_3, respectively. The method is applied to the determination of hydroxyamino-acid content of complete protein hydrolysates. Silk fibroin has, relatively, low (I) and high (II) content.

IV. The hydroxyamino-acid fraction prepared from a wool hydrolysate by the acetylation–benzoylation procedure is investigated. Low recoveries of threonine are obtained; nearly 2% of the N of wool is isolated as optically active serine.

V. The acetylation–benzoylation procedure is applied to the lysine fractions of gelatin and isinglass hydrolysates, when a picrate, explodes at 226—227°, is obtained (Van Slyke *et al.*, A., 1938, III, 757). The "hydroxylysine" is probably αε-diamino-δ-hydroxyhexoic acid; with HIO_4 it affords NH_3 and CH_2O. A. T. P.

VIII.—ANALYSIS.

Rapid determination of the nitrogen content of organic compounds by the Dumas method. T. Nishi (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 432—434B).—Shortening of the time required for an analysis depends mainly on the use of a Therex glass combustion tube which enables partial avoidance of loss of time during heating and cooling. H. W.

Determination of sulphur in organic compounds by hydrogenation. W. Theilacker and W. Schmid (*Angew. Chem.*, 1940, **53**, 255—256; *Gas- u. Wasserfach*, 1940, **83**, 601).—Ter Meulen's method for determining S in org. compounds by catalytic cracking and hydrogenation to H_2S has been improved and simplified. In the examination of substances containing N and halogens the method has the advantage over the method of combustion followed by volumetric determination of the H_2SO_4 formed in that it can be applied to all substances. A weighed sample is slowly evaporated in a stream of H_2 in a quartz or supremax tube, and the vapours are passed at red heat through platinised quartz wool on which S compounds are quantitatively converted into H_2S, which is absorbed in aq. AcOH containing $Zn(OAc)_2$. The ZnS formed is determined iodometrically. R. B. C.

Analytical procedures employing Karl Fischer reagent. VI. Determination of carbonyl compounds. J. Mitchell, jun., D. M. Smith, and W. M. D. Bryant (*J. Amer. Chem. Soc.*, 1941, **63**, 573—574; cf. A., 1939, I, 577).—A new analytical procedure for aldehydes and ketones is given. The H_2O formed in the reaction between CO compounds and NH_2OH,HCl in presence of C_5H_5N is determined by titration with Karl Fischer reagent. Results for 21 aldehydes and ketones are given; camphor only does not react completely. The effect of interfering substances is discussed. W. R. A.

Iodometric determination of the sum of aldol and *p*-aldol in acetaldehyde. M. Hori (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 52—54).—The method depends on the fact that *p*-aldol is decomposed to aldol by $NaHSO_4$, and that aldol combines with $NaHSO_4$ in acid, and separates again in slightly alkaline, solution. J. N. A.

Semimicro-determination of copper reduced by sugars. T. G. Phillips (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 181—183).—A modification of Bertrand's method is described. F. O. H.

Reduction of cystine at the dropping mercury electrode.—See A., 1941, I, 216.

Photocolorimetric determination of tannins. M. Rosenblatt and J. V. Peluso (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 170—181).—The blue colour developed by the Folin–Denis reagent (Na phosphotungstate–phosphomolybdate) was analysed by quartz spectrograph–photometer apparatus and the procedure established for attainment of max. transmission and stability compatible with good sensitivity. The method gives an error ⩾0·5%. F. O. H.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

JULY, 1941.

I.—ALIPHATIC.

Photolysis of ethyl iodide in various solvents [and determination of ethyl iodide].—See A., 1941, I, 275.

Cadmium-photosensitised reactions of propane.—See A., 1941, I, 275.

Kinetics of oxidation of hydrocarbons.—See A., 1941, I, 270.

Chromium oxide gel catalysts for dehydro-cyclisation of *n*-heptane.—See A., 1941, I, 274.

High-pressure chlorination of paraffins.—See B., 1941, II, 133.

Catalytic polymerisation of ethylene at atmospheric pressure. XI. Influence of hydrogen and nitrogen. XII. Action of acetylene. Y. Konaka (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 363B; cf. B., 1938, 762).—XI. The presence of H_2 diminishes the yield of polymeride oil over Ni, Co, or Fe catalysts. N_2 acts merely as a diluent.

XII. C_2H_2 alone yields little oil but $C_2H_2 + H_2$ (1 : 1) give a good yield of mainly aromatic oil, of lower distillation range than the oil from C_2H_4, which is paraffinic. Although present in the polymerisation products of C_2H_4, C_2H_2 is not to be regarded as the main intermediate product. A. R. PE.

Catalytic polymerisation of ethylene at atmospheric pressure. IX, X.—See B., 1941, II, 134.

Polymerisation of olefines. III. Polymeric olefines from methyl*iso*propylcarbinol. F. C. Whitmore and W. A. Mosher (*J. Amer. Chem. Soc.*, 1941, **63**, 1120—1123; cf. A., 1941, 756).—$CHMePr^{\beta}\cdot OH$ and 75% H_2SO_4 at 76—80° give (cf. Drake *et al.*, A., 1934, 1329). $CHMeBu^{\gamma}\cdot CMe{:}CHMe$ (45), $CMe_2Et\cdot CH_2\cdot CMe{:}CHMe$ (I) (35), C_2HMe_3 (1), $CMeEt{:}CHMe$ (3), $COMePr^{\beta}$ (1), $CHMeBu^{\gamma}\cdot CMe{:}CH_2$ (2), other nonenes (1), and higher polymerides (5%). Reaction mechanisms are postulated. $COMe\cdot CH_2\cdot CMe_2Et$ and MgMeI give $CMe_2Et\cdot CH_2\cdot CMeEt\cdot OH$, b.p. 86°/30 mm., dehydrated by 75% H_2SO_4 at 80° to a 20 : 1 and by $CuSO_4$ to a 6 : 1 mixture of (I) and $CMe_2Et\cdot CH{:}CMeEt$. $COMe\cdot CHMeBu^{\gamma}$ and $COEt\cdot CHMeBu^{\gamma}$ do not react with MgRI. R. S. C.

Property of conjugated systems. J. Kenner (*Nature*, 1941, **147**, 482).—In a compound $X\cdot[CH{:}CH]_n\cdot Y$ the conjugated system is an electronic conductor between the covalent groups X and Y, and there must be a correspondence between such chemical properties of the compound as leave the conjugated system intact and those of the covalent compound XY. The val. of this generalisation as a means of insight into the reactivity, and its mechanism, of the compound XY has been overlooked. Its bearing on the nitration of paraffins, the mechanism of nitrosation of $NHMe_2$, and the mechanism of certain inorg. reactions is discussed. L. S. T.

Absorption spectrum of squalene.—See A., 1941, I, 192.

Removal of substituents from vinyl polymerides. II. F. T. Wall (*J. Amer. Chem. Soc.*, 1941, **63**, 821—824; cf. A., 1940, II, 202).—The removal of Cl from polyvinyl chloride or a co-polymeride of vinyl chloride and acetate by Zn is treated statistically when the polymeride is made up of "head to head–tail to tail" units. The results are compared with previously derived equations for structures involving 1–2 or 1–3 removal of Cl_2. It is proved rigorously that different removal rates of 1–2 and 1–3 Cl_2 pairs have no effect on the final % of Cl in a randomly oriented polymeride. W. R. A.

Catalytic dehydration and dehydrogenation of butyl and amyl alcohol. V. I. Komarewsky and J. T. Stringer (*J. Amer. Chem. Soc.*, 1941, **63**, 921—922).—Passage of $Bu^{\alpha}OH$, *n*- or *iso*-$C_5H_{11}\cdot OH$ over Al_2O_3–Cr_2O_3 (cf. A., 1939, II, 491) at 575—625°/128—155 mm. (apparatus described) gives 20·4—49·3% of olefine (dehydration by Al_2O_3), 1·8—15·9% of diene [$(CH_2{:}CH)_2$, $CHMe{:}CH\cdot CH{:}CH_2$, or isoprene, respectively; mixed dehydration–dehydrogenation], considerable amounts of aldehyde (dehydrogenation by Cr_2O_3; decomposed during the reaction to CO, CO_2, and paraffins), and free C. Over Al_2O_3 alone more olefine is formed but no diene. R. S. C.

Use of methylallyl chloride in the synthesis of compounds with conjugate unsaturation. C. D. Hurd and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1941, **63**, 976—977).—$CH_2{:}CMe\cdot CH_2Cl$ (I) and HOCl give *ββ′-dichloro*-tert.-*butyl alcohol*, b.p. 72—73°/23 mm., converted by KCN in hot aq. MeOH into $(CN\cdot CH_2)_2CMe\cdot OH$, an oil, which with HCl–abs. EtOH gives an OH-ester and thence by distillation with I yields $CO_2Et\cdot CH_2\cdot CMe{:}CH\cdot CO_2Et$ (*α-CHPh·* derivative, softens at ~170°, decomp. 175—200°). With aq. Br–KBr or I–HgO, (I) gives *β-chloro-β′-bromo-*, b.p. 84—85°/20 mm., and *-β′-iodo*-tert.-*butyl alcohol*, b.p. 101—103° (decomp.)/18 mm., respectively. R. S. C.

Effect of zinc chloride on octyl alcohol. M. M. Gerasimov and V. E. Glushnev (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 462—465).—Interaction of octyl alcohol (I) vapour at 225—325° with $ZnCl_2$ distributed on pumice gives hexenes, heptenes, octenes, $CMe_2{:}CH_2$, $CHMe{:}CH_2$, C_2H_4, and H_2 and saturated hydrocarbons due to "cracking" of (I). The yield of H_2 and unsaturated hydrocarbons is the greater the higher is the temp. Aldehydes are present in the fractions of high b.p. J. L. D.

Preparation of αγ-butylene glycol from aldol by high-pressure hydrogenation. I. Reaction with nickel catalyst prepared electrolytically. II. Reaction with mixed catalyst of nickel and alumina. H. Nagai (*J. Soc. Chem. Ind. Japan*, 1941, **44**, 41—43B, 43B).—Aldol has been hydrogenated to $OH\cdot CHMe\cdot[CH_2]_2\cdot OH$, varying the temp., time, amount and pressure of H_2, and amount of catalyst. Optimum results are obtained with 10% of catalyst and a H_2–aldol ratio >77 : 23 by vol., at 80° and >30 atm. pressure.

II. Addition of Al_2O_3 to the catalyst reduces the reaction rate and the yield. A. LI.

Catalytic preparation and interconversion of simple and mixed esters. V. N. Ipatieff and R. L. Burwell, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 969—971).—Passage of MeOH over "solid H_3PO_4" at 350°/55 atm. gives 86—87% of Me_2O. At 336°/60 atm. MeOH + EtOH gives similarly Me_2O, MeEtO, and Et_2O (largely decomposed to C_2H_4). MeOH + $CH_2Ph\cdot OH$ at 350°/50 atm. gives similarly $CH_2Ph\cdot OMe$. $Me_2O + Et_2O$ are decomposed by the catalyst at 450°. In an autoclave Me_2O and Et_2O are equilibrated by the catalyst at 150°. R. S. C.

Structure of the Cori ester. M. L. Wolfrom and D. E. Pletcher (*J. Amer. Chem. Soc.*, 1941, **63**, 1050—1053).—The structure of the Cori ester (I) as *d*-glucopyranose 1-phosphate is confirmed. Synthetic (I) (Cori *et al.*, A., 1938, II, 39) has $[\alpha]^{20}_{5892\cdot5}$ +78°, $[\alpha]^{20}_{5461}$ +90° in H_2O, is hydrolysed by 5% HCl at 60° to glucose (isolated as Et_2 mercaptal penta-acetate), and is characterised as K_2 salt, $+2H_2O$ [mol. wt. (cryoscopy; H_2O) normal; does not reduce Fehling's solution], which consumes 2 HIO_4 giving 1 HCO_2H and no CH_2O. R. S. C.

Cetyl 3 : 5-dinitrobenzoate, m.p. 72·3°.—See A., 1941, III, 367.

Absorption of oxygen by mercaptans in alkaline solution. J. Xan, E. A. Wilson, L. D. Roberts, and N. H. Horton (*J. Amer. Chem. Soc.*, 1941, **63**, 1139—1141).—RSH in aq. NaOH absorb more O_2 than is required for formation of R_2S_2 (reason unknown). The rate of absorption of O_2 increases with the concn. of alkali, when allowance is made for decrease in the solubility of O_2 in the solution. The rate of absorption is R = Pr^a > Bu > *n*-amyl > CH_2Ph > Ph. R. S. C.

Sulphonation of *iso*butylene. I. β-Methylpropene-αγ-disulphonic acid and related compounds. C. M. Suter and J. D. Malkemus (*J. Amer. Chem. Soc.*, 1941, **63**, 978—981).—Addition of SO_3 (4·38) and then of *iso*-C_4H_8 (2·2) to dioxan (3 mols.) in $(CH_2Cl)_2$ at 0°, warming to 50°, and keeping at 0° gives 30% of *dioxan β-methylpropene-αγ-disulphonate* (**I**), whence the *Ba* (**II**), +5H_2O (1 H_2O retained at 115°/10 mm.; unsaturated to $KMnO_4$), Na_2, $(NH_4)_2$, and $(NH_2Ph)_2$ (**III**) salts are prepared. $SOCl_2$ converts (**I**) into the acid *anhydride* (**IV**), m.p. 167—170°, which is only slowly hydrolysed by H_2O or aq. alkali, reacts only slowly with Br–CCl_4 or –H_2O, and with NH_2Ph in EtOAc gives (**III**). PCl_5 at 100° converts (**IV**), (**I**), or (**II**) into the *disulphonyl chloride* (**V**), m.p. 79·2—79·8°, which gives the *diamide*, m.p. 152·5—154°, and *dianilide*, m.p. 171·5—172·5°, at 180—210° gives SO_2 and (?) $CH_2Cl{\cdot}CMe{:}CHCl$, and with 3 : 5-$(NO_2)_2C_6H_3{\cdot}CO_2Ag$ gives products, m.p. 56—57° and 139—142° (not derived from *cis*- or *trans*-$OH{\cdot}CH_2{\cdot}CMe{:}CHCl$). $CH_2Cl{\cdot}CMe{:}CH_2$ and 2·25% HOCl at ~15° give $OH{\cdot}CMe(CH_2Cl)_2$ and thence by aq. Na_2SO_3 at 70—90°, followed by PCl_5 at 100°, (**V**). Hydrogenation of (**III**) to $CHMe(CH_2{\cdot}SO_3NH_3Ph)_2$ [prepared from $CHMe(CH_2Cl)_2$] failed. SO_3–dioxan and Bu$^\gamma$OH at 0—5° give dioxan H sulphate and only a trace of org. acid. R. S. C.

Radioactive carbon as tracer in synthesis of propionic acid from carbon dioxide by propionic acid bacteria.—See A., 1941, III, 536.

Thermal transformations of thallous formate.—See A., 1941, I, 278.

Substituted acetylenes and their derivatives. XLII. Preparation, properties, and derivatives of α-acetylenic acids. A. O. Zoss and G. F. Hennion (*J. Amer. Chem. Soc.*, 1941, **63**, 1151—1153; cf. Campbell amd Eby, A., 1941, **II**, 81).—C_2HNa in liquid NH_3 at −35° is treated with RBr and then with $NaNH_2$ at −45°. The resulting crude CR:CNa is treated in Et_2O, C_6H_6, or PhMe with CO_2 at −50° and then with saturated aq. $NaHSO_4$, giving thus good yields of CR:C·CO_2H with 5% of C_2R_2. CR:C·CO_2Me (prep. by H_2SO_4–MeOH) with HgO–Et_2O,BF_3–$CCl_3{\cdot}CO_2H$–MeOH gives $OMe{\cdot}CR{:}CH{\cdot}CO_2Me$ (purified by distillation with a trace of *p*-$C_6H_4Me{\cdot}SO_3H$), with liquid NH_3–MeOH gives CR:C·$CO{\cdot}NH_2$, and with $NHPh{\cdot}NH_2$ at 130° gives the pyrazolone. Addition of Br to the acid in CCl_4 gives $CRBr{:}CBr{\cdot}CO_2H$. Thus are obtained Δ$^\alpha$-*n*-pentinenoic, m.p. 50·0° [*dibromide*, m.p. 35—38·5°, b.p. 126°/6 mm. (another fraction containing 66·42% of Br had m.p. 40·2—43·7°, b.p. 118—125·5°/6 mm.); Me ester, b.p. 47°/10 mm.; *amide*, m.p. 146—146·5°], -hexinenoic, m.p. 24·5—25°, b.p. 111°/10 mm. (Me ester, b.p. 65°/10 mm.; *dibromide*, b.p. 125°/2 mm.; *amide*, m.p. 81·5—82°), -heptinenoic, b.p. 122°/10 mm. (Me ester, b.p. 72°/10 mm.; *dibromide*, b.p. 142°/7 mm.; *amide*, m.p. 68—69°), and -octinenoic acid, b.p. 133°/10 mm. (Me ester, b.p. 94°/10 mm.; *dibromide*, b.p. 146°/2 mm.; *amide*, m.p. 89—90°), *Me β-methoxy-*Δ$^\alpha$*-n-pentenoate*, b.p. 59·5°/10 mm., *-hexenoate*, b.p. 76°/10 mm., *-heptenoate*, b.p. 88°/10 mm., and *-octenoate*, b.p. 100°/10 mm., 1-phenyl-3-ethyl-, m.p. 100—110·5°, *-n*-propyl-, m.p. 110·5—111°, *-n-butyl-*, m.p. 83—83·5°, and *-n*-amyl-, m.p. 95·5—96°, -pyrazolone. R. S. C.

Synthesis of Δ$^\alpha$-pentadecenoic and -heptadecenoic acids. W. M. Lauer, W. J. Gensler, and E. Miller (*J. Amer. Chem. Soc.*, 1941, **63**, 1153—1155).—The following general synthesis is devised, increasing the C chain by one unit. $CH_2R{\cdot}CO_2H \rightarrow CHRBr{\cdot}CO_2H \rightarrow$ (+KOH) $OH{\cdot}CHR{\cdot}CO_2H \rightarrow$ [+Pb(OAc)$_4$–AcOH; 60°] RCHO (obtained also, less well, by pyrolysis) $\rightarrow$ [+$CH_2(CO_2H)_2$–C_5H_5N at room temp. and later 100°] $CHR{:}CH{\cdot}CO_2H$. Thus are obtained *n*-$C_{12}H_{25}{\cdot}CHO$, b.p. 150—155°/28 mm. (semicarbazone, m.p. 105·5—106·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 107—108°), *n*-$C_{14}H_{29}{\cdot}CHO$, b.p. 155—160°°/12—14 mm. (semicarbazone, m.p. 108—109°; 2 : 4-*dinitrophenylhydrazone*, m.p. 107·5—108°), Δ$^\alpha$-*heptadecenoic*, m.p. 57·5° (*amide*, m.p. 110—110·5°; p-*bromoanilide*, m.p. 115—116°), and *-pentadecenoic acid*, m.p. 47·5—48° (*amide*, m.p. 111·5—112·5°; p-*bromoanilide*, m.p. 114—114·5°). The structure of the acids is proved by ozonolysis in $CHCl_3$ to give RCHO. R. S. C.

Chemistry of fatty acids. VII. Multiple nature of linoleic and linolenic acids prepared by the bromination-debromination procedure. Purification of these acids by repeated low-temperature crystallisation. N. L. Matthews, W. R. Brode, and J. B. Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 1064—1067; cf. A., 1940, II, 266).—Debromination of linoleic (**I**) and linolenic (**II**) acid bromides and crystallisation of the products from light petroleum at ~ −60° shows the presence of ~12 and ~15%, respectively, of isomerides in the products, whence existence of isomerides in the "natural" acids is inferred. (**I**), m.p. −5·2° to −5·0°, and (**II**), m.p. −11·3° to −11·0° (hexabromide no. 96·0), are reported. R. S. C.

Geometric isomerism of linolenic acids. Elaidolinolenic acid. J. P. Kass, J. Nichols, and G. O. Burr (*J. Amer. Chem. Soc.*, 1941, **63**, 1060—1063).—Heating the Et esters of the acids from linseed oil with Sc–N_2 at 205—215°, followed by hydrolysis and treatment with Br, gives *elaidolinolenic acid hexabromide* (**I**), m.p. 169—170° (Et ester, m.p. 114—115°), and Et_2O-sol. bromides. Zn and HCl–EtOH convert (**I**) into Et elaidolinolenate, b.p. 138°/1 mm., hydrolysed to the *acid* (**II**), m.p. 29—30°, f.p. 29·5—30°, I val. (Wijs) 271·8, and CNS val. 149·7 (absorbs 3 H_2). Pure (**II**) gives only 31% of (**I**), whence it follows that formation of more than one bromide from linolenic acid is not evidence for existence of a β-isomeride. R. S. C.

Malonatomanganiates.—See A., 1941, **I**, 278.

Hydrogen bridges and isomerism. H. C. Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 882—883).—Polemical against Reimer *et al.* (A., 1940, II, 374; 1941, II, 102). W. R. A.

Wound hormones of plants. V. Synthesis of analogues of traumatic acid. J. English, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 941—943; cf. A., 1940, III, 271).—Et H sebacate and boiling $SOCl_2$ give the ester *chloride*, b.p. 129—130°/1 mm., and thence by H_2–Pd in xylene (no "poison") Et θ-aldehydo-*n*-nonoate, b.p. 130°/2 mm. Condensation of $CO_2H{\cdot}[CH_2]_n{\cdot}CHO$ and $CH_2(CO_2H)_2$ by C_5H_5N at room temp. and subsequent hydrolysis by 2N-NaOH–EtOH gives $CO_2H{\cdot}[CH_2]_n{\cdot}CH{:}CH{\cdot}CO_2H$ and some $CO_2H{\cdot}[CH_2]_{n-1}{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H$ (*A*), but by $NPhMe_2$–MeOH or $N([CH_2]_2{\cdot}OH)_3$ gives mainly (*A*); the isomerides are best separated by adsorption on C from Et_2O. Thus are obtained Δ$^\alpha$-*nonene-αι-*, m.p. 103°, *-n*-decene-*ακ-*, m.p. 165°, and *-n-tridecene-αν-*, m.p. 108·5°, Δ$^\beta$-*n*-nonene-*αι-*, m.p. 90°, *-n-decene-ακ-*, m.p. 109°, and *-tridecene-αν-dicarboxylic acid*, m.p. 104°. $([CH_2]_3{\cdot}CHBr{\cdot}CO_2Et)_2$ (prep. from the acid chloride by Br, followed by EtOH) with $NPhMe_2$ at 180° gives Δ$^{\alpha\eta}$-*octadiene-αθ-dicarboxylic acid*, m.p. 236—239° (decomp.), hydrogenated (1 mol. of H_2; Pt; EtOH) to Δ$^\alpha$-*n-octene-αθ-dicarboxylic acid*, m.p. 173°. $CO(CH_2{\cdot}CO_2Et)_2$, $I{\cdot}[CH_2]_4{\cdot}CO_2Et$, and NaOEt–EtOH give an undistillable ester, which in boiling conc. HCl gives *n-undecan-ζ-one-αλ-dicarboxylic acid*, m.p. 114° (*Et* ester, b.p. 180°/0·5 mm.), hydrogenated (PtO_2; 30—40 lb.; Et_2O–EtOH) to *n-undecan-ζ-ol-αλ-dicarboxylic acid*, m.p. 102—103°, which with PI_3 at 100° gives an oily I-acid, converted by 25% KOH–EtOH into Δ$^\epsilon$-*n-undecene-αλ-dicarboxylic acid*, m.p. 72°. *n-Nonan-ε-one-*, m.p. 111°, and *n-nonan-ε-ol-αι-dicarboxylic acid*, m.p. 95°, but not the unsaturated acid, are similarly prepared. Other methods of prep. failed. The unsaturated acids are all plant wound hormones, more active than the saturated acids. M.p. are corr. R. S. C.

Crystalline sodium salt of pantothenic acid. N. Gätzi-Fichter, H. Reich, and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 185—187).—*Na pantothenate*, m.p. 121—122°, $[\alpha]_D^{13}$ +29°±1·5° in H_2O, is obtained from the Ba salt and Na_2SO_4 with subsequent crystallisation from EtOH with addition of $COMe_2$ or Et_2O or by addition of α-hydroxy-ββ-dimethylbutyrolactone to NaOMe–MeOH containing β-alanine. It is very hygroscopic. *Na* l-*pantothenate* has m.p. 120—122°, $[\alpha]_D^{15}$ −27·4°±2·5° in H_2O. H. W.

Use of Bunte salts in synthesis. II. Preparation of derivatives of thiol-aliphatic acids. G. G. Stoner and G. Dougherty (*J. Amer. Chem. Soc.*, 1941, **63**, 987—988; cf. A., 1940, II,

159).—$CH_2Cl·CO_2Na$ and aq. $Na_2S_2O_3$ give $SO_3Na·S·CH_2·CO_2Na$, oxidised by I in hot H_2O to $(S·CH_2·CO_2H)_2$. *dl*-$(CHMeBr·CO_2Na)_2$ gives similarly $(S·CHMe·CO_2H)_2$, and $Cl·[CH_2]_2·CO_2H$ gives $(S·[CH_2]_2·CO_2H)_2$. $Cl·[CH_2]_3·CN$ with $Na_2S_2O_3$ in boiling EtOH and later I gives *di-γ-thiolbutyronitrile* (70%), an oil, hydrolysed by hot conc. HCl to $(S·[CH_2]_3·CO_2H)_2$. $CO_2H·[CH_2]_n·S·SO_3Na$ (prep. as above) with HCl and RCHO or COR_2 gives *S*-methylene-, m.p. 126—127° (cf. lit.), *S*-benzylidene-, m.p. 124° (cf. lit.), *S-o*-nitrobenzylidene-, m.p. 124° (lit. 122—123°), and *S-iso*propylidene-di(thiolacetic acid), m.p. 129° (cf. lit.), *S*-methylene- m.p. 149—152° (lit. 155—156°), *S*-benzylidene-, m.p. 149—150° (lit. 138—140°), S-iso*propylidene*-, m.p. 174°, and S-*α'-methylpropylidene-di-(α-thiolpropionic acid)*, m.p. 126—127°, S-*methylene*-, m.p. 142°, S-*benzylidene*-, m.p. 90°, and S-iso*propylidene-di-(β-thiolpropionic acid)*, m.p. 70°.

R. S. C.

δ-Valerosultone. T. Nilsson (*Svensk Kem. Tidskr.*, 1940, **52**, 324—325).—$Br·[CH_2]_4·SO_3Na$ in aq. $AgNO_3$ at 55° for 4 hr. gives *δ-valerosultone* (I), liquid, polymerising on keeping. Hydrolysis of (I) in dil. aq. solution at 60° is unimol. and is thus not catalysed by H^+.

M. H. M. A.

[Photolytic] reactions of the acetyl radical.—See A., 1941, I, 276.

Photolysis of glyoxal and acetaldehyde.—See A., 1941, I, 276.

High-temperature photolysis of acetone and the action of free methyl radicals on propane.—See A., 1941, I, 276.

Synthesis of methyl vinyl ketone by hydration of vinylacetylene under pressure.—See B., 1941, II, 135.

Acetylene derivatives. XIV. Synthesis of ββ-dialkyldivinyl ketones by isomerisation of *tert.*-vinylethylcarbinol. XV. Vinyl ketones and their polymerisation. I. N. Nazarov. XVI. Action of ethylene oxide on vinylethinylcarbinols. Esterification of β-hydroxyethyl ethers of vinylethinylcarbinols with organic acids. I. N. Nazarov and V. M. Romanov (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1940, 545—551, 552—558, 559—570).—XIV. The general reaction $OH·CRR'·C{:}C·CH{:}CH_2 + R''OH \rightarrow OR''·CH_2·CH_2·CO·CH{:}CRR'$ takes place in presence of $HgSO_4$ (12 hr. at 35—40°) (R'' = Me, R = R' = Me, Et, Pr^a; R = *Me*, R' = *Et*, b.p. 91—93°; R = Me, R' = Pr^a; RR' = $[CH_2]_5$). When heated with *p*-$C_6H_4Me·SO_3H$ the keto-ethers eliminate R''OH, yielding the ketones $CH_2{:}CH·CO·CH{:}CRR'$ (R = R' = Me, *Et*, b.p. 59—60°/5 mm., *Pr^a*, b.p. 80—81°/5 mm.; R = *Me*, R' = *Et*, b.p. 50—51°/6 mm., R' = *Pr^a*, b.p. 73—74°/10 mm.; RR' = $[CH_2]_5$, b.p. 98·5—101°/12 mm.). The ketones are hydrogenated to the saturated ketones, $COEt·CH_2·CHRR'$ [R = R' = Me, *Et*, b.p. 179—181° (*carbazone*, m.p. 127—128°), *Pr^a*, b.p. 209—211° (*semicarbazone*, m.p. 89—90°); R = *Me*, R' = *Et*, b.p. 161—162° (*carbazone*, m.p. 92—93°), R' = *Pr^a*, b.p. 178—180° (*semicarbazone*, m.p. 64—65·5°)].

XV. The keto-ethers described above are hydrogenated (Pt catalyst) to keto-ethers, $OMe·CH_2·CH_2·CO·CH_2·CHRR'$, which when distilled from *p*-$C_6H_4Me·SO_3H$ give ketones, $CH_2{:}CH·CO·CH_2·CHRR'$ (R = R' = *Me*, b.p. 41—42°/22 mm., *Et*, b.p. 65—66°/11 mm., *Pr^a*, b.p. 90—91°/12 mm.; R = *Me*, R' = *Et*, b.p. 40—41°/7 mm.; R = *Me*, R' = *Pr^a*, b.p. 72—73°/16 mm.; RR' = $[CH_2]_5$, b.p. 96°/12 mm.). The ketones readily polymerise to elastic, transparent products.

XVI. Carbinols of the type $OH·CRR'·C{:}C·CH{:}CH_2$ are obtained by condensation of ketones CORR' with $CH{:}C·CH{:}CH_2$ (R = R' = Me, *Pr^a*, b.p. 83°/4 mm.; R = Me, R' = Et; R = Me, R' = Pr^a; RR' = $[CH_2]_5$). The carbinols condense with 1 or 2 mols. of $(CH_2)_2O$ to yield the mono- and di-glycyl ethers, $OH·CH_2·CH_2·O·CRR'·C{:}C·CH{:}CH_2$ [R = R' = *Me*, b.p. 80—81°/4 mm. (*acetate*, b.p. 92—93°/5 mm.; *propionate*, b.p. 102—104°/4 mm.; *butyrate*, b.p. 110—113°/4 mm.; iso*butyrate*, b.p. 98—100°/2·5 mm.; *valerate*, b.p. 120—121°/4 mm.); R = R' = *Pr^a*, b.p. 108—109°/3 mm.; R = *Me*, R' = *Et*, b.p. 89—90°/5 mm. (*butyrate*, b.p. 129—131°/4 mm.); R = *Me*, R' = *Pr^a*, b.p. 96—97°/4 mm.; RR' = $[CH_2]_5$, b.p. 118—119°/3 mm.], and $OH·CH_2·CH_2·O·CH_2·CH_2·O·CRR'·C{:}C·CH{:}CH_2$ (R = R' = *Me*, b.p. 103—104°/2 mm.; R = R' = *Pr^a*, b.p. 140—142°/4 mm.; R = *Me*, R' = *Et*, b.p. 125—127°/4 mm.; R = *Me*, R' = *Pr^a*, b.p. 135—137°/4 mm.; RR' = $[CH_2]_5$, b.p. 149—150°/3 mm.). All the above products polymerise on keeping to transparent gels, the tenacity of which falls with increasing mol. wt. of R and R'.

R. T.

Photolysis of diacetyl in the near ultra-violet.—See A., 1941, I, 276.

Preparation of *d*-mannose. H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1941, **26**, 47—48).—The prep. from ivory nut shavings is described in detail.

J. W. S.

***iso*Propylidene derivative of the mercaptals of monosaccharides. VI. Crystalline 2-methyl-*d*-mannose and its α-methylglucofuranoside, dimethyl acetal, and dibenzyl mercaptal.** E. Pacsu and S. M. Trister (*J. Amer. Chem. Soc.*, 1941, **63**, 925—928; cf. A., 1940, II, 365).—The "4-"methylmannose (I) of Pacsu *et al.* (A., 1930, 70) is shown to be the 2-derivative (cf. Munro *et al.*, A., 1936, 826) and the structure of intermediates is modified accordingly. Mannose $(CH_2Ph)_2$ mercaptal (modified prep. from α-methyl-*d*-mannofuranoside) gives the (mainly 3 : 4-5 : 6-)$(CMe_2)_2$ derivative, a syrup, $[\alpha]_D^{21}$ +59·5° in $(CHCl_2)_2$, converted by NaOMe–MeI (twice) into the syrupy 2-Me derivative, whence conc. HCl in boiling 80% EtOH yields 83% of 2-methylmannose $(CH_2Ph)_2$ mercaptal (II), m.p. 117°, $[\alpha]_D^{21}$ −43·1° in C_5H_5N, +39·5° in $CHCl_3$. With HgO–$HgCl_2$ in MeOH at 60°, (II) gives *2-methyl-α-methylmannofuranoside* (III), m.p. 82°, $[\alpha]_D^{25}$ +129·5° in H_2O, with a little *2-methylmannose Me_2 acetal* (IV), m.p. 111—112°, $[\alpha]_D^{21}$ −11·3° in H_2O. N-HCl at 100° hydrolyses (III) to (I), m.p. 136—137° (lit. a syrup), $[\alpha]_D^{20}$ +7·0° → +4·5° in 24 hr. in H_2O, which, according to the conditions, yields phenylglucosazone or *2-methylmannose-phenylhydrazone*, m.p. 163°, [α] −49·1° → −60·7° in 24 hr. in C_5H_5N. Hydrolysis of (IV) by 0·05N-HCl at 21° gives 2-methyl-α- and -β-methylmannofuranoside (increased lævorotation) and then more slowly (I). The data of Pacsu *et al.* (*loc. cit.*) for (II) probably refer in error to the glucose analogue.

R. S. C.

Hydrolysis of turanose in alkaline solution. H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1941, **26**, 35—46).—Treatment of turanose (I) with aq. $Ca(OH)_2$ at 20° leads to a decrease in rotation, the final val. being in accord with the view that hydrolysis occurs to glucose and *d*-fructose instead of the normal Lobry de Bruyn interconversion. A solution of (I) in N-KOH turns brown and becomes lævorotatory, the loss in [KOH] according with the view that the hydrolysis products enolise and decompose to yield saccharic acids. Alkaline oxidation of 0·17 mol. of fructose yields 2·9 g. and of (I) 1·8 g. of cryst. K *d*-arabate (II). Lactulose yields no (II) but forms the K salt of a dibasic acid, presumably 3-β-*d*-galactopyranosido-*d*-arabonic acid. These differences in behaviour and the differences in Cu-reducing vals. are discussed with reference to the effect of the glycosidic linking on the behaviour of the sugars in alkaline solution.

J. W. S.

[Degradation of long-chain molecules.] H. Mark and R Simha (*Trans. Faraday Soc.*, 1941, **37**, 244).—A note on a recent paper by the authors (cf. A., 1940, II, 268).

F. L. U.

Separation of starch into its two constituents. E. Pacsu and J. W. Mullen (*J. Amer. Chem. Soc.*, 1941, **63**, 1168—1169).—When an adsorbent (best, cotton; also activated C, fuller's earth, or Al_2O_3) is added to cold 1% maize-starch paste, the amylose is adsorbed. Cold H_2O then removes the α-amylose (I), which can be recovered by pptn. by EtOH. Final elution with hot H_2O extracts the β-amylose (II) giving a clear aq. solution, which rapidly ppts. a degraded, insol. form; pptn. by EtOH gives a similar material. Addition of C_5H_5N during distillation of the aq. solution of (II) gives a solution of (II) in C_5H_5N, whence (II) is pptd. by EtOH. (I) and (II) have $[\alpha]_D^{20}$ +145° in 20% NaOH and differ only in that (*a*) (I) contains 0·020% of P and (II) contains no P, and (*b*) (I) gives a purple and (II) a deep blue colour with I.

R. S. C.

Fractionation of wheat starch.—See B., 1941, III, 68, 98, 150.

Starch. IX. Degradation by β-amylase and the law of mass action. K. H. Meyer and J. Press (*Helv. Chim. Acta*, 1941, **24**, 50—58).—The degradation of sol. starch (I) (Zulkowski) by β-amylase is a reaction of zero order; until degradation has reached 35—40% the quantity of maltose (II) formed in unit time is const. In conc. solution [0·6—1·4% of (I)] this is not remarkable but the concn. of terminal groups may be considered const. in more dil. solution in which concn. has a marked influence on the rate of reaction. The evidence points to the existence of an additive compound

of enzyme and substrate in equilibrium with its products of dissociation. The reaction is inhibited by (II). In alkaline solution (p_H 4·8) amylose from maize or potato starch is degraded ~65% as rapidly as (I). H. W.

Starch. XI. Residual dextrin from maize starch (erythrogranulose). K. H. Meyer, M. Wertheim, and P. Bernfeld (*Helv. Chim. Acta*, 1941, **24**, 212—216).—Amylopectin (I), obtained by the cautious removal of amylose from maize starch, is solubilised by CCl_3·$CH(OH)_2$ and subjected to the action of β-amylase (II) in H_2O; all the terminal groups of (I) are found in the residual dextrin (III). Possibly the very slow attack of (II) on (III) is due to the liberation of maltose or glucose. H. W.

Starch. X. Degradation of glycogen by β-amylase. K. H. Meyer and J. Press (*Helv. Chim. Acta*, 1941, **24**, 58—62).—Glycogen (I) obtained by Brücke's method is much more slowly attacked than sol. starch by β-amylase (II) but with a high concn. of enzyme it is possible to achieve 45% degradation with formation of 55% of residual dextrin. Lyoglycogen, isolated without use of alkali and containing about ⅓ its wt. of protein (III), is not attacked by (II) in a solution which has been made alkaline and then neutralised. If (III) is removed by tungstic acid the residual (I) is more rapidly attacked than Brücke's (I). H. W.

Factors in the methylation of cellulose acetate and of cellulose dissolved in benzyltrimethylammonium hydroxide. G. G. Johnston (*J. Amer. Chem. Soc.*, 1941, **63**, 1043—1050).—The amount of methylation of cellulose acetate (I) achieved in one operation increases as the degree of polymerisation decreases. Repeated methylation gives products containing 1% less OMe than theoretical for trimethylation. Higher OMe is achieved only after reacetylation, which involves further depolymerisation. Only in $COMe_2$ is methylation of (I) easier than that of cellulose. Fine division increases the ease of methylation. Methylation and deacetylation in $COMe_2$ are initially slow, owing to the immiscibility of $COMe_2$ with conc. NaOH, but accelerate as the product ppts. and thus comes in contact with NaOH. In CH_2Ph·NMe_3·OH the reaction rate is normal as the solution is homogeneous, but methylation ceases at ~43% of OMe owing to insolubility of the product. Cohesive forces (H or OH linkings) are responsible for the incomplete methylation. R. S. C.

Amination in liquid ammonia.—See B., 1941, II, 134.

Treatment of simple aliphatic amines with nitrous acid. F. C. Whitmore and R. S. Thorpe (*J. Amer. Chem. Soc.*, 1941, **63**, 1118—1120; cf. A., 1932, 1022).—Yields of ROH from NH_2R and HNO_2 are R = Me 0, Et 60, Pr$^\alpha$ 7, and Pr$^\beta$ 32% (also 28% of C_3H_6) with traces of Et and Pr ethers. Failure of the reaction with NH_2Me is due to hydrolysis of the nitrite occurring more readily than its decomp. R. S. C.

Reductive alkylation of ammonia and amines with aldehydes and ketones. Preparation of ethylamines from acetaldehyde.—See B., 1941, II, 135.

Manufacture of amino-fatty acid derivatives.—See B., 1941, II, 137.

Molecular refraction of ions of *l*-aspartic acid.—See A., 1941, I, 194.

Azlactones. HI. Acylation of amino-acids in pyridine. H. E. Carter, P. Handler, and C. M. Stevens (*J. Biol. Chem.*, 1941, **138**, 619—626).—70% yields of acetyl-, *butyryl*-, m.p. 86—87°, iso*butyryl*-, m.p. 105—106°, *valeryl*-, m.p. 84—85°, *γ-methylvaleryl*-, m.p. 129—130°, and *trimethylacetyl-phenylalanine*, m.p. 124—125°, and the corresponding *acyl*-dl-*valines*, m.p. —, 148—149°, 165—167°, 105—106°, 144—146°, and 98—99°, are obtained from the NH_2-acid and acid chloride in C_5H_5N below 40°. *dl*-Valine with BzCl in C_5H_5N gives a mixture of benzoyl-*dl*-valine and -*dl*-valylvaline, m.p. 170—205°. Leucine behaves similarly. Benzoyl-*dl*-phenylalanine with BzCl or (poor yield) AcCl or Ac_2O yields the azlactone, which with NH_2Ph affords the anilide. Benzoyl-*dl*-alanyl-, *acetyl*-dl-*phenylalanyl*-, m.p. 211—212°, and n-*valeryl*-dl-*valyl*-*anilide*, m.p. 164—165°, are similarly prepared. Benzoyl-*dl*-phenylalanylglycine, m.p. 225—237°, and n-*valeryl*-dl-*valyl*-dl-*valine*, m.p. 180—183°, are obtained in poor yield from the azlactone and NH_2-acid in C_5H_5N at room temp. A. Li.

Synthesis of β-hydroxynorvaline. M. Botvinnik, E. Morozova, and G. Samsonova (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **30**, 133—136).—Equimol. amounts of Δ$^\alpha$-pentenoic acid (I) with $Hg(OAc)_2$ in cold MeOH give a mixture of Hg derivatives of β-methoxyvaleric acid which when treated with aq. KBr–Br gives α-bromo-β-methoxyvaleric acid (II), converted by 25% aq. NH_3 under pressure at 100° for 2 hr. into α-amino-β-methoxyvaleric acid, which with boiling 48% HBr gives β-hydroxynorvaline (cf. Abderhalden *et al.*, A., 1934, 638). (I) with $AgNO_3$ and Br in MeOH at 5—15° gives (II) (cf. West *et al.*, A., 1938, II, 129). J. L. D.

Benzoylation of amino-acids. H. E. Carter and C. M. Stevens (*J. Biol. Chem.*, 1941, **138**, 627—629).—*l-p*-Methoxyphenylalanine with excess of BzCl in aq. $NaHCO_3$ gives the partly racemised Bz derivative (I) (75—85%), and an oil hydrolysed to BzOH and (I). Similar products are obtained from *dl*-alanine and *dl-O*-methyl*allo*threonine. Bz derivatives of > 16 NH_2-acids, and some β-phenylpropionyl derivatives, have been prepared without racemisation in 0·5N-NaOH. An explanation of this difference is suggested. A. Li.

Sulphur in proteins. VI. Alkaline decomposition of cysteine. H. V. Lindstrom and W. M. Sandstrom (*J. Biol. Chem.*, 1941, **138**, 445—450).—Uvitic, uvitonic, and thiolacetic acids are produced by the action of boiling 2N-$Ba(OH)_2$ on cysteine (I), or on a mixture of its primary decomp. products, $AcCO_2H$, H_2S, and NH_3. The residue after extraction of the products from (I) with Et_2O and then boiling alkaline $Pb(OAc)_2$ contains alanine (II), which stabilises (I) in NaOH or KOH, but not in $Ba(OH)_2$. It is concluded that (II), when formed, condenses with $AcCO_2H$ in presence of NaOH or KOH, inhibiting further decomp. of (I). A. Li.

Dehydration of hydroxy-amino-acids. M. M. Botvinnik, M. A. Prokofiev, and N. D. Zelinski (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **30**, 129—132).—β-Hydroxyvaline (I) (1 mol.) with Bz_2O (3 mols.) at 150°/1 hr. gives the azlactone (II) of α-benzamido-β-methylcrotonic acid (III), hydrolysed (N-NaOH at 100°) to (III). When (II) is boiled with N-HCl for 5·5 hr., $COPr^\beta$·CO_2H is formed. (III) gives (II) on brief boiling with Ac_2O, or when heated with Bz_2O at 120—125° for 20 min. The sulphate of (I) is not dehydrated when fused with Bz_2O. Similarly, α-amino-β-hydroxybutyric acid, or its Bz derivative, with Bz_2O yields the azlactone, m.p. 95° (cf. Carter *et al.*, A., 1939, II, 423), hydrolysed (N-NaOH at 80°) to α-benzamidocrotonic acid, m.p. 193—195°. J. L. D.

New sulphur-containing amino-acid (lanthionine) from sodium carbonate-treated wool. M. J. Horn, D. B. Jones, and S. J. Ringel (*J. Biol. Chem.*, 1941, **138**, 141—149).—Hydrolysis (conc. HCl) of wool previously boiled with 2% aq. Na_2CO_3, concn. of the hydrolysate, and pptn. of the EtOH solution of the residue with C_5H_5N yields *ββ′-diamino-ββ′-dicarboxydiethyl sulphide* (*lanthionine*), decomp. 304° (softening at 270°) (NN′-*Bz*$_2$ derivative, m.p. 205—206°), with two other compounds with similar properties and the same N content. A. Li.

Synthesis of new sulphur-containing amino-acid [lanthionine] isolated from sodium carbonate-treated wool. V. du Vigneaud and G. B. Brown (*J. Biol. Chem.*, 1941, **138**, 151—154).—Cysteine (from cystine and Na in liquid NH_3) with CH_2Cl·$CH(NH_2)$·CO_2Me,HCl and KOH yields lanthionine (preceding abstract) [NN′-*dicarbobenzyloxy*-derivative, m.p. 138—140° (corr.)]. A. Li.

High-pressure reduction of fatty acid amides. II. S. Ueno and S. Takase (*J. Soc. Chem. Ind. Japan*, 1941, **44**, 29—30B).—The amides of palmitic (I), hexoic, octoic, stearic, lauric, and myristic acid have been hydrogenated in dioxan to the corresponding *sec.* amines [*e.g.*, C_7H_{15}·CO·NH_2 → $(C_8H_{17})_2NH$], varying temp., pressure, time, and quantity of catalyst (Cu–Cr_2O_3 with a trace of Ba) and of solvent. Optimum results are obtained at 270—290°/180—200 atm. for 1 hr., with 3 times as much dioxan as amide. From (I) n-*cetylamine* (*hydrochloride*, m.p. 130—133°) is also obtained. With little or no solvent the amides decompose. A. Li.

Action of halogens on αβ-unsaturated ureides. C. J. Cavallito and C. S. Smith (*J. Amer. Chem. Soc.*, 1941, **63**, 995—998).—*trans*-CHMe:CH·COCl and $CO(NH_2)_2$ in CCl_4 give trans-*crotonylcarbamide*, which with Br–CCl_4 at 0—5° gives a *dibromide*, m.p. 150°. trans-*Cinnamylcarbamide* and aq. Br give the *dibromide*, m.p. 180°. Maleamic and maleic acids

also give dibromides (*αβ*-dibromosuccinamic acid has m.p. 170°), but *succinuric acid* does not react. Maleuric acid (I) with Br in H_2O or CCl_4 at 0—10° gives *β-bromomaleuric acid* (II), m.p. 147°, hydrolysed by H_2O at room temp. to *β-hydroxymaleuric acid* (III), m.p. 230—270°. With Br–H_2O at 30—35°, (I), (II), or (III) gives *tribromopyruvylcarbamide* (IV), m.p. 260° [N-*Cl*-derivative (V), m.p. 210°; N-*Ag* salt, with alkali gives $CHBr_3$]. I does not react with (I). IBr and (I) in H_2O at 0—10° give *β-iodomaleuric acid*, m.p. 150—155°, converted by IBr at 30° into *tri-iodopyruvylcarbamide*, m.p. 220° [also obtained from (II) by IBr], and by Br into (IV). (IV) is a mild sedative and (V) is antiseptic. M.p. are corr. (decomp.). R. S. C.

Sebacic acid mononitrile. B. S. Biggs and W. S. Bishop (*J. Amer. Chem. Soc.*, 1941, **63**, 944).—Distillation of $([CH_2]_4{\cdot}CO{\cdot}NH_2)_2$ (crude or pure) or $([CH_2]_4{\cdot}CO_2NH_4)_2$ gives 50—55% of $([CH_2]_4{\cdot}CN)_2$, b.p. 204°/16 mm., and 35% of *ι-cyano-n-nonoic acid* (I), m.p. 51·5—52° (purified by way of the Ba salt). With NaOMe–Me_2SO_4–MeOH (I) gives *Me ι-cyano-n-nonoate* (II), b.p. 178°/16 mm. $CO_2H{\cdot}[CH_2]_8{\cdot}CO_2Me$ with $SOCl_2$ and then aq. NH_3 gives *Me n-decoamate*, m.p. 77·4°, which with P_2O_5 in boiling $(CHCl_2)_2$ gives (II). R. S. C.

Purification of lecithin.—See A., 1941, III, 368.

Dimethyl silicon dichloride and methyl silicon trichloride. W. F. Gilliam, H. A. Liebhafsky, and A. F. Winslow (*J. Amer. Chem. Soc.*, 1941, **63**, 801—803).—*Si* Me_2 *dichloride*, b.p. 69·0—70·2°/744·5 mm., and *Si Me trichloride*, b.p. 66·2—67°/765·8 mm., have been prepared by a Grignard reaction between MgMeCl and $SiCl_4$ in Et_2O and Bu^a_2O respectively. W. R. A.

Polymeric methyl silicon oxides. E. G. Rochow and W. F. Gilliam (*J. Amer. Chem. Soc.*, 1941, **63**, 798—800).—Polymeric Si Me oxides (I) have been prepared by direct hydrolysis of the product obtained by action of MgMeBr on $SiCl_4$, and by hydrolysis of mixtures of $SiMeCl_3$ and $SiMe_2Cl_2$. (I) are intermol. condensation products of Me silicols. The properties and thermal stability of the products obtained by using various Me/Si ratios are recorded. Resins prepared by both methods are identical, and appear to consist essentially of a siloxane network in which Me are attached directly to Si. W. R. A.

Redistribution reaction. X. Relative affinity of mercury and lead for methyl and ethyl radicals. G. Calingaert, H. Soroos, and H. Shapiro (*J. Amer. Chem. Soc.*, 1941, **63**, 947—948; cf. A., 1940, II, 295).—Equilibration of $HgMe_2$ (2) with $PbEt_4$ (3 mols.) by $AlCl_3$ gives a random equilibrium mixture, for which the relative affinity const. is 3·4 in good agreement with that (4·5±0·4) determined previously (A., 1940, II, 300) for a mixture in different proportions. R. S. C.

II.—HOMOCYCLIC.

Catalytic dehydrogenation of *cyclo*pentane in presence of chromic oxide.—See A., 1941, I, 273.

Mechanism of catalytic hydrogenation of phenol under high pressure. VII. Comparison of hydrogenated products of *cyclo*hexanol and *cyclo*hexane. S. Andō (*J. Soc. Chem. Ind. Japan*, 1940, **43**, 355—356B; cf. B., 1938, 903).—Both *cyclo*hexane (I) and *cyclo*hexanol (II) when hydrogenated at 380°/200 atm. over MoS_3 produced methyl*cyclo*pentane (III), the yield from (II) being > that from (I), and it is concluded that *cyclo*hexene rather than (I) is the intermediate in the conversion of (II) into (III), whilst (II) is an intermediate in the hydrogenation of PhOH. A. R. Pe.

***cis–trans*-Isomeric stilbenes. V. Stereoisomeric forms of 2 : 4′-dinitrostilbene; phenanthrene syntheses. III.** P. Ruggli and A. Dinger (*Helv. Chim. Acta*, 1941, **24**, 173—185).—Protracted heating of *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2Na$ and *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ with Ac_2O and $ZnCl_2$ at 70° gives 2′ : 4-*dinitrostilbene-7-carboxylic acid* (I), m.p. 185°; piperidine as condensing agent causes evolution of CO_2. Reduction (Raney Ni–EtOH–EtOAc) of (I) gives 2′ : 4-*diaminostilbene-7-carboxylic acid*, m.p. 186° (Ac_2 derivative, m.p. 240°), converted by diazotisation and subsequent boiling with EtOH into phenanthrene-9-carboxylic acid, m.p. 252° (yield 18%). Decarboxylation of (I) in quinoline containing Cu chromite at 220° gives a mixture from which cis-2′ : 4-*dinitrostilbene* (II), m.p. 140°, is isolated. (II) (or the mixture) is not appreciably affected by boiling HCl–EtOH, quinoline, or $PhNO_2$ but with $PhNO_2$ containing a trace of I at 205—210° yields pure trans-2′ : 4-*dinitrostilbene* (III), m.p. 140°. (II) is reduced (Raney Ni in EtOAc) to cis-2′ : 4′-*diaminostilbene* (IV), m.p. 105° (Ac_2 derivative, m.p. 180°), transformed into phenanthrene. 2′ : 4 : 4′-Trinitrostilbene is reduced by $(NH_4)_2S$ in EtOH to 2′ : 4-*dinitro-4′-aminostilbene*, m.p. 202° (*hydrochloride*; *Ac* derivative, m.p. 237°), converted by diazotisation and boiling with EtOH into (III), catalytically reduced (Raney Ni in EtOAc) to trans-2′ : 4-*diaminostilbene*, m.p. 125—126° (Ac_2 derivative, m.p. 241°). This, when diazotised and then boiled with EtOH containing a little Cu powder, yields stilbene. It is also obtained by isomerisation of (IV) by slow distillation under 13 mm. Bromination of (III) in $CHCl_3$ affords a 73% yield of a *dibromide* (V), m.p. 212°, and an uncrystallisable resin. Under similar conditions (II) gives (V) in 16% yield with a resin from which a *bromide*, m.p. 165°, could be isolated in small amount. Warm C_5H_5N transforms (V) into (III) in 72% yield. Passage of Cl_2 through (III) in boiling $CHCl_3$ gives a *dichloride* (VI), m.p. 125—126°, whereas a *dichloride*, m.p. 204°, is derived from a mixture of (II) and (III). (VI) is converted by NaOH into a *substance*, $C_{14}H_8O_{2\cdot5}N_2$, m.p. 244°, probably owing to ring formation. H. W.

Synthesis of tricyclic hydrocarbons related to stilbœstrol. A. A. Plentl and M. T. Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 989—995).—Slow addition of indan-1-one (I) in Et_2O to $CH_2Ph{\cdot}MgCl–Et_2O$ gives 65% of 1-*benzylideneindane* (purified by adsorption of impurities on Al_2O_3), b.p. 157—157·5°/2 mm., which probably contains 1-benzylindene since only poor yields of BzOH and (I) are obtained by $KMnO_4$ in aq. K_2CO_3 and $COMe_2$, respectively. CHPhMeBr and CN·CPhNa·CO_2Et (II) in hot EtOH give *Et α-cyano-αβ-diphenyl-n-butyrate*, b.p. 157°/0·2 mm., and some CHPhMe·CHPh·CN, m.p. 133° (lit. 129—130°), both converted by 1 : 2 HCl–AcOH at 200° into $CHPhMe{\cdot}CHPh{\cdot}CO_2H$, forms, m.p. 186° (lit. 181°) (*amide*, m.p. 193°) and 135° (lit. 133—134°) (*amide*, m.p. 173—174°), which with boiling $SOCl_2$, followed by $AlCl_3$ in CS_2, gives 2-*phenyl-3-methylindan-1-one*, m.p. 86° (2 : 4-*dinitrophenylhydrazone*, m.p. 204°; no semicarbazone), converted by MgEtI–Et_2O, followed by Ac_2O, into 2-*phenyl-3-methyl-1-ethylindene*, an oil. $Ph{\cdot}[CH_2]_2{\cdot}Br$ and (II) in dioxan give *Et α-cyano-αγ-diphenyl-n-butyrate*, b.p. 174—175°/0·5 mm., and thence, as above, *αγ-diphenyl-n-butyric acid*, m.p. 76°, and 1-*keto*-2-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 79° (2 : 4-*dinitrophenylhydrazone*, m.p. 204°; no semicarbazone), 1-*hydroxy*-2-*phenyl*-1-*ethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 129°, and 2-*phenyl*-1-*ethyl*-3 : 4-*dihydronaphthalene*, b.p. 80—90° (bath)/0·1 mm. Attempts to condense CHPhMe·MgBr and (I) failed, since only $(CHPhEt)_2$ was obtained. R. S. C.

Formation of ions from compounds with conjugated double bonds: hydrocarbon salts. J. Weiss (*Nature*, 1941, **147**, 512; cf. A., 1940, II, 247).—Salts of coronene, 1 : 2-benzperylene, 3 : 4-benzpyrene, and anthracene with ClO_4', SO_4'', and P_2O_7'''' as anions have been prepared from the hydrocarbon and an oxidising agent [CrO_3, $K_3Fe(CN)_6$, or H_2O_2] in presence of the moderately conc. acids at room temp. Deeply coloured, H_2O-sol. salts are formed even from the sulphonated hydrocarbons. *Anthracene perchlorate* (I), $[C_{14}H_{10}]^+[ClO_4]'$, m.p. >110° (decomp.), gives dark brown crystals (absorption spectrum in $COMe_2$ given). H_2O decomposes (I), but not the salts of the higher-mol. hydrocarbons. The deep colour of the solutions is due to the positive hydrocarbon ion, and univalent ions, [hydrocarbon]$^+$[anion]$'$, have been observed. The well-known hydrocarbon polynitro-compounds are present to an appreciable extent as ionic compounds of the type [hydrocarbon]$^+$[NO_2-compound]$'$ and [NH_2-compound]$^+$-[NO_2-compound]. L. S. T.

1-Methylphenanthrene. I. Conversion of retene into 1-methylphenanthrene. T. Hasselstrom (*J. Amer. Chem. Soc.*, 1941, **63**, 1164—1165).—1-Methylphenanthrene [derived phenazine, new m.p. 183·5° (corr.)] (with propylene and an oily by-product) is obtained (97 g.) by boiling retene (250 g.) with dehydrated fuller's earth and thus becomes readily available. R. S. C.

Syntheses in the phenanthrene and triphenylene series. L. F. Fieser and W. H. Daudt (*J. Amer. Chem. Soc.*, 1941, **63**, 782—788).—*dl*-$(CHMe{\cdot}CO)_2O$ (I), m.p. 88—89°, b.p. 234—237° (prep.: Bone *et al.*, J.C.S., 1899, **75**, 839), and

1-$C_{10}H_7$·MgBr in boiling Et_2O–C_6H_6–N_2 give mixed *β*-1-*naphthoyl-α-methyl*-n-*butyric acids* (**II**) (66·5%; the Friedel–Crafts reaction is less satisfactory), whence a small amount of a pure *acid*, m.p. 151·2—151·4°, is isolated. (**II**) enolises readily and in HCl–AcOH or $-Ac_2O$ at room temp. or with boiling HCl–MeOH gives *γ*-1-*naphthyl-αβ-dimethyl*-Δ*β*-*crotonolactone*, m.p. 96—97°, which reduces Tollens' reagent but gives no Legal reaction. Hydrogenation (Cu chromite; 140°/1500—2500 lb.) of the Na salt of (**II**) in H_2O gives 81·5% of *γ*-1-*naphthyl-αβ-dimethyl*-n-*butyric acid*, *forms*, m.p. 107·5—108·5° and 114—115°, cyclised by HF to 1-*keto*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (**III**) (88·5%), an oil, whence a small amount of crystals, m.p. 91—98°, is obtained. Clemmensen–Martin reduction and dehydrogenation (Pd–C; 300—330°) converts (**III**) into 2 : 3-dimethylphenanthrene (**IV**). MgMeBr and (**III**) in C_6H_6 give a carbinol, which with Pd–C at 300°, later 300—350°, gives 1 : 2 : 3-*trimethylphenanthrene* (42·5%), m.p. 63·8—64·8° [picrate, m.p. 187—188°; $C_6H_3(NO_2)_3$ compound, m.p. 200·7—201·5°]. 2-$C_{10}H_7$·MgBr and (**I**) give similarly *β*-2-*naphthoyl-α-methyl*-, m.p. 149—153° (*enol lactone*, m.p. 126—127·5°), and *γ*-2-*naphthyl-αβ-dimethyl*-n-*butyric acid*, m.p. 83—84°, and thence by HF or, probably better, $ZnCl_2$–Ac_2O, 4-*keto*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (**V**), m.p. 93·4—94·5° after softening. Interaction of crude (**V**) with MgMeBr, dehydration at 200°, and removal of adsorbable (Al_2O_3) material gives an oil, which with Pd–C gives 17% of 2 : 3 : 4-*trimethylphenanthrene*, m.p. 62·8—63·8° [picrate, m.p. 113—114°; $C_6H_3(NO_2)_3$ compound, m.p. 139—140°]. Al(OPr*β*)$_3$ reduces (**V**) in PhMe to 4-*hydroxy*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 111—114·5° [dehydrogenated to (**IV**)], converted by HCl–C_6H_6 into the chloride, which with $CH_2(CO_2Et)_2$ and NaOEt–EtOH–C_6H_6 and later boiling 40% KOH gives 2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-4-*phenanthrylmalonic acid*, m.p. 188—190° (gas). Heating at 200° then gives 2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*-4-*phenanthrylacetic acid*, m.p. 110—123°, cyclised by HF to 1-*keto*-3 : 4-*dimethyl*-1 : 2 : 2a : 3 : 4 : 5-*hexahydropyrene*, *forms*, m.p. 204·5—206·5° and 197—202°. Mg 9-phenanthryl bromide and (**I**) give, as above, *β*-9-*phenanthroyl-α-methylbutyric acid*, m.p. 170—171·5° (slight previous softening) [picrate, m.p. 176—177°; $C_6H_3(NO_2)_3$ compound, m.p. 188·5—189·2°; *enol lactone*, m.p. 216—218°], *γ*-9-*phenanthryl-αβ-dimethyl*-n-*butyric acid*, m.p. 158—163° [$C_6H_3(NO_2)_3$ compound, m.p. 174—175·5°], 1-*keto*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrotriphenylene* (**VI**), m.p. 132—138°, 1 : 2 : 3-*trimethyltriphenylene*, m.p. 109·8—110·6° [picrate, m.p. 186—186·5°; $C_6H_3(NO_2)_3$ compound, m.p. 203·7—204·1°], (by Zn–Hg–PhMe–HCl) 2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydrotriphenylene* (**VII**), m.p. 158—167° [picrate, m.p. 154—158°; $C_6H_3(NO_2)_3$ compound, m.p. 158—160°], [from (**VII**) by Pd–C] 2 : 3-*dimethyltriphenylene* (**VIII**), m.p. 156·7—157·2° [$C_6H_3(NO_2)_3$ compound, m.p. 237—237·7°], and [from (**VI**) by Pd–C, which gives also some (**VIII**)] 1-*hydroxy*-2 : 3-*dimethyltriphenylene*, m.p. 167·5—168·5° [$C_6H_3(NO_2)_3$ compound, 239—240°; picrate, m.p. 210·5—211·5°]. 1-$C_{10}H_7$·CH:CHMe and (:CH·CO)$_2$O at 100° give (?) 3-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*-1 : 2-*dicarboxylic anhydride* (77·5%), m.p. 271·8—272°, unaffected by HCl–AcOH–Ac_2O and dehydrogenated by S to 3-*methylphenanthrene*-1 : 2-*dicarboxylic anhydride*, m.p. 332—333°. M.p. are corr. R. S. C.

Action of acids on *β*-hydroxy-sulphonamides. T. L. Cairns and J. H. Fletcher (*J. Amer. Chem. Soc.*, 1941, **63**, 1034—1035).—*iso*Butylene oxide (**I**) and boiling aq. NH_3 give OH·CMe$_2$·CH$_2$·NH$_2$ (**II**). Steam-distillation of the *N*-*p*-C_6H_4Br·SO_2 derivative of (**II**) with 75% H_2SO_4 or 48% HBr gives *p*-C_6H_4Br·SO_2·NH_2 and Pr*β*CHO (isolated as *methone* derivative, m.p. 148—150°) (cf. A., 1939, II, 496). *β*-*p*-*Bromobenzenesulphonyl*-tert.-*butyl alcohol*, m.p. 89—90·5°, gives similarly EtCHO, but *p*-C_6H_4Br·SO_2·NH·[CH$_2$]$_2$·OH is unaffected. The fission is catalysed by acid, since it is not effected by P_2O_5 or AcCl. R. S. C.

Catalytic reduction of nitrobenzene in the liquid phase.—See B., 1941, II, 173.

Reductive alkylation of hindered aromatic primary amines. W. S. Emerson, F. W. Neumann, and T. P. Moundres (*J. Amer. Chem. Soc.*, 1941, **63**, 972—974).—Reductive alkylation of NH_2Ar by RCHO (cf. A., 1940, II, 11) in acid media can be accomplished if polymeride formation is prevented by substitution of Ar at positions 2, 4, and 6. Zn–Hg–AcOH–conc. HCl is an effective reducing agent. Thus, mesidine with CH_2O gives 2 : 4 : 6 : 1-$C_6H_2Me_3$·NMe_2 (**I**) (70%) [*hydrochloride*, m.p. 155—156° (decomp.); also obtained similarly from 2 : 4 : 6 : 1-$C_6H_2Me_3$·NO_2 (**II**)], with RCHO gives *N-iso*butyl- (91%), b.p. 267—277° [*hydrochloride*, m.p. 148—150° (decomp.); *Ac* derivative, m.p. 71·5—72·5°], and *N-iso*amyl-mesidine (94%), b.p. 155—165°/20 mm. [*Bz* derivative, m.p. 92—93°; hydrochloride, an oil; also obtained from (**II**) (61%)], and with COMe$_2$ gives 18% of *N-iso*propylmesidine, b.p. 118—123°/3 mm. NH_2Ph gives similarly 31% of NHPhPr*β*. (**I**) is also obtained by using HCO_2H as reducing agent, which, however, fails in other cases. R. S. C.

Synthesis and toxicity of N^1-*p*-fluorophenylsulphanilamide. G. P. Hager, E. B. Starkey, and C. W. Chapman (*J. Amer. Pharm. Assoc.*, 1941, **30**, 65—68).—*p*-NO_2·C_6H_4·N_2·BF_4 (from *p*-NO_2·C_6H_4·N_2Cl and $NaBF_4$; cf. Dunker *et al.*, A., 1937, II, 39) is converted into *p*-C_6H_4F·NO_2 and thence *p*-C_6H_4F·NH_2, which with *p*-NHAc·C_6H_4·SO_2Cl in COMe$_2$–C_5H_5N affords the N^4-Ac derivative, m.p. 190°, of N^1-*p*-fluorophenylsulphanilamide (**I**), m.p. 166·5° (corr.) (sinters 162—165°, softens 165°) (cf. Suter *et al.*, A., 1940, II, 164). For toxicity of (**I**), cf. A., 1941, III, 526. F. O. H.

Phosphoric acid derivatives of sulphanilamides.—See B., 1941, III, 161.

4-Aminodiphenyl-4′-sulphonamide. C. K. Donnell, J. H. Dietz, and W. T. Caldwell (*J. Amer. Chem. Soc.*, 1941, **63**, 1161—1162).—*p*-C_6H_4Ph·NO_2 and $ClSO_3H$ at, successively, <15°, room temp., and 60° give *p*-NO_2·C_6H_4·C_6H_4·SO_2Cl-*p* (94%), m.p. 178°, and thence the amide, which is reduced by Sn–HCl–EtOH to *p*-NH_2·C_6H_4·C_6H_4·SO_2·NH_2-*p*, m.p. 263° (corr.). R. S. C.

Reaction of aldehydes with amines. III. *N′*-Acetyl-*NN*-dibenzyl-*m*-phenylenediamine. F. G. Singleton and C. B. Pollard (*J. Amer. Chem. Soc.*, 1941, **63**, 998—999).—*m*-NH_2·C_6H_4·N(CH$_2$Ph)$_2$ (A., 1941, II, 102) with RCHO gives Schiff's bases, but with Ac_2O at room temp. affords N′-*acetyl*-NN-*dibenzyl*-m-*phenylenediamine*, m.p. 228°, 4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamidotriphenylmethane*, m.p. 228°, 4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamido*-3″ : 4″-*dimethoxy*-, m.p. 231°, -2″-, m.p. 244°, and -4″-*methoxy*-, m.p. 224°, -3″-, m.p. 216°, and -4″-*methyl*-, m.p. 218°, -3″ : 4″-*methylenedioxy*-, m.p. 225°, and -4″-*hydroxy*-3″-*methoxy*-, m.p. 196°, -*triphenylmethane*, 2″-, m.p. 239°, 3″-, m.p. 211°, and 4″-*nitro*-, m.p. 251°, 2″-, m.p. 242°, and 4″-*chloro*-, m.p. 248°, and 2″-*chloro*-5″-*nitro*-, m.p. 240°, -4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamidotriphenylmethane*, 4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamidodiphenylmethane*, m.p. 241°, αα-4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamidodiphenylcthane*, m.p. 172°, -*propane*, m.p. 230°, -n-*butane*, m.p. 245°, and -n-*hexane*, m.p. 201°, and α-*phenyl*-ββ-4 : 4′-*bisdibenzylamino*-2 : 2′-*diacetamidodiphenylethane*, m.p. 184°. Small amounts of Schiff's bases, acridines, and CRR′$_2$·OH are also formed. M.p. are corr. R. S. C.

Isomerism of diazoaminoazo-compounds. F. P. Dwyer (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 169—174; cf. A., 1939, II, 543).—Diazoaminoazobenzene, purplish-red quinonoid form (**I**), PhN$_2$·N:C$_5$H$_4$:N·NHPh, m.p. 121—122°, is obtained by neutralising *p*-NPh:N·C_6H_4·N_2Cl with Na_2CO_3, and coupling with NH_2Ph. (**I**) dissolves in C_5H_5N to a deep red solution, and addition of light petroleum then gives (after 2—3 days) brownish-yellow needles, m.p. 138—139°, of the triazen *form* (**II**), PhN$_2$·NH·C_6H_4·N_2Ph, m.p. 138—139°, which is best obtained by allowing a saturated solution of (**I**) in amyl acetate to evaporate slowly. A mixture of (**I**) and (**II**) melts at 142—143° (softens at 138°), indicating probable salt formation between the acidic (**I**) and feebly basic (**II**). When a solution of the crude salt from (**I**) or (**II**) and MeOH–NaOAc–$AgNO_3$–C_5H_5N in C_5H_5N at 85° is cooled to 25°, the orange-yellow *Ag* salt (**III**), decomp. 200—205°, of (**II**), separates. When a solution of (**III**) in C_5H_5N at 85° is cooled rapidly to 20°, filtered, and the filtrate mixed with MeOH at −10°, the *Ag* salt (**IV**), probably dimeric, m.p. 195—200° (explodes at 205°), of (**I**) separates. (**III**) or (**IV**) and MeI–COMe$_2$ afford the same *N*-Me derivative, m.p. 84—85°. A. T. P.

Reactivity of phenols towards paraformaldehyde.—See A., 1941, I, 214.

2-Nitro-4-*tert.*-alkylphenols.—See B., 1941, II, 178.

2 : 5-Dialkylphenols.—See B., 1941, II, 177.

Polymorphic forms of substituted phenols. R. T. Arnold, H. Klug, J. Sprung, and H. Zaugg (*J. Amer. Chem. Soc.*, 1941, **63**, 1161).—Forms, m.p. 53—54° and 62° (stable), of 5 : 6 : 7 : 8-tetrahydro-β-naphthol and, m.p. 39·5—40° and 49—50° (stable), of 4-hydrindenol are prepared by alkali fusion of the Na sulphonates and from the diazonium salts, respectively. R. S. C.

Exploration of methods for preparation of stilbene derivatives. II. Unsymmetrical stilbenes. W. H. Linnell and H. S. Shaikmahamud (*Quart. J. Pharm.*, 1941, **14**, 64—72; cf. A., 1940, II, 167).—*p*-OMe·C_6H_4·[CHBr]$_3$·CO_2H [from *p*-OMe·C_6H_4·CH:CH·CO_2H, prep. of which by Knoevenagel's reaction gives a little of (?) *p*-OMe·C_6H_4·CH:C$(CO_2H)_2$, m.p. 204°] with dry PhOH at >50°/30 mm., followed by treatment of the product with aq. Na_2CO_3, affords *4'-hydroxy-4-methoxystilbene* (**I**), m.p. 209—210° [*acetate*, m.p. 167—168° (opaque), 182—183° (clear)], and 41·3% of (probably) p-*hydroxy-β-p'-anisylcinnamic acid*, m.p. 185—186° (*Me ether Me ester*, m.p. 86—87°, hydrolysed to the *Me ether*, m.p. 137—138°), presumably formed by addition of PhOH to *p*-OMe·C_6H_4·C:C·CO_2H. *Et β-hydroxy-β-p-acetoxyphenyl-α-ethylvalerate*, m.p. 85° (from *p*-OAc·C_6H_4·COEt, CHBrEt·CO_2Et, and Zn in C_6H_6), with $SOCl_2$–C_5H_5N in dry Et_2O yields Et *p*-acetoxy-αβ-diethylcinnamate, b.p. 162—164°/5 mm. (from which no stilbene derivative could be obtained by heating its dibromide with PhOH), hydrolysed by 25% MeOH–KOH to p-*hydroxy-αβ-diethylcinnamic acid*, m.p. 133° (**II**) and 119—121° (probably *cis*- and *trans*-forms); (**II**) is methylated to p-*methoxy-αβ-diethylcinnamic acid* (**III**), m.p. 63—64°. *Et β-hydroxy-β-p-anisyl-α-ethylvalerate*, m.p. 71—72° (from *p*-OMe·C_6H_4·COEt as above), similarly yields (**III**) (mixture of isomerides). (**III**) and the corresponding *p*-OAc-compound give dibromides which decompose on removal of solvent; bromination of (**III**) and direct addition of PhOH, however, gives an *acid*, m.p. 125—126° [probably either *p*-OMe·C_6H_4·C(:CHMe)·CEtBr·CO_2H or *p*-OMe·C_6H_4·CEtBr·C(:CHMe)·CO_2H]. (*p*-OMe·C_6H_4·CH:)$_2$ (**IV**) is obtained by methylation of (**I**) and from *p*-OMe·C_6H_4·N_2Cl, *p*-OMe·C_6H_4·CH:CH·CO_2H, and 33% aq. $CH_2Cl·CO_2Na$ in boiling $COMe_2$; the corresponding stilbene derivative could not be similarly obtained from (**III**) (both forms) or *p*-OH·C_6H_4·CH:CH·CO_2H. (**I**), (**IV**), (*p*-OH·C_6H_4·CH:)$_2$, new m.p. 288—289° [from (**IV**) and Na in $C_2H_4(OH)_2$], and its diacetate were examined for œstrogenic activity (cf. A., 1941, III, 509). F. O. H.

Structures of arylhydrazones of unsymmetrieally substituted quinones. L. I. Smith and W. B. Irwin (*J. Amer. Chem. Soc.*, 1941, **63**, 1036—1043).—*m*-Cresol and *p*-NO_2·C_6H_4·N_2Cl (**I**) in aq. NaOH give *4'-nitro-4-hydroxy-2-methylazobenzene*, m.p. 163—164° (*acetate*, m.p. 132—133°), reduced by $Na_2S_2O_4$ in aq. EtOH to 2 : 1 : 5-NH_2·C_6H_3Me·OH, which is oxidised, best by steam-distillation with $Fe_2(SO_4)_3$, to *p*-toluquinone (**II**). *o*-Cresol and (**I**) give *4'-nitro-4-hydroxy-3-methylazobenzene* (**III**), m.p. 205—206° (decomp.) (*acetate*, m.p. 144·5—146°), also obtained (in only 28% yield, cf. below) from (**II**) by *p*-NO_2·C_6H_4·NH·NH_2 (**IV**), and reduced by $Na_2S_2O_4$ to 5 : 1 : 2-NH_2·C_6H_3Me·OH. *s-m*-Xylenol and (**I**) give 4'-nitro-4-hydroxy-2 : 6-dimethylazobenzene, m.p. 167—168° (decomp.) (*acetate*, m.p. 133—133·5°), and thence 2 : 1 : 3 : 5-NH_2·$C_6H_2Me_2$·OH, m.p. 179—180° (decomp.) [lit. 180·5—181·5° (decomp.)], oxidised by $Fe_2(SO_4)_3$ to *m*-xyloquinone (**V**) and by $FeCl_3$ to 3-*chloro*-2 : 6-*dimethyl-p-benzoquinone*, m.p. 55·5—57°. (**IV**) and (**V**) give *4'-nitro-4-hydroxy-3 : 5-dimethylazobenzene* (77%), m.p. 182—183° (decomp.) (*acetate*, m.p. 192—193°), reduced by $Na_2S_2O_4$ to 5 : 1 : 3 : 2-NH_2·$C_6H_2Me_2$·OH. 1 : 3 : 4 : 5-$C_6H_2Me_3$·OH (**VI**) and *p*-NO_2·C_6H_4·N_2HSO_4 (**Ia**) (prep. by *iso*-C_5H_{11}·O·NO) in AcOH give *4'-nitro-4-hydroxy-2 : 3 : 6-trimethylazobenzene* (68% at 10°; 90%, less pure, in H_2O), m.p. 165·5—166·5° (decomp.) (*acetate*, m.p. 133—134°), reduced to 3 : 1 : 2 : 4 : 6-NH_2·C_6HMe_3·OH. ψ-Cumoquinone (**VII**), (**IV**), and H_2SO_4 in EtOH give *4'-nitro-4-hydroxy-2 : 3 : 5-trimethylazobenzene* (73%), m.p. 227—228° (decomp.) (*acetate*, m.p. 165°), reduced to *6-amino-ψ-cumenol* [*4-amino-2 : 3 : 6-trimethylphenol*], m.p. 136—137° (decomp.) (*hydrochloride*, chars slightly ~225°), which with $FeCl_3$ gives (**VII**), isolated as quinol diacetate. Durenol and (**Ia**) in AcOH at 14—15° give 94% and duroquinone (**VIII**) and (**IV**) give 53% of *4'-nitro-4-hydroxy-2 : 3 : 5 : 6-tetramethylazobenzene*, m.p. 174—174·5° (decomp.) (*acetate*, m.p. 143—144°), reduced to *aminodurenol*, m.p. 177—178·5° [179—183° (decomp.)], which gives (**VIII**) by oxidation. 2 : 4 : 1-$(NO_2)_2C_6H_3$·N_2Cl (**IX**) and (**VI**) in AcOH at 15—16° give 2' : 4'-*dinitro-4-hydroxy-2 : 3 : 6-trimethylazobenzene*, m.p. 188·5—189° (decomp.) (*acetate*, m.p. 155—156°), whence reduction and then oxidation gives only a trace of (**VII**). (**VII**) with 2 : 4 : 1-$(NO_2)_2C_6H_3$·NH·NH_2 (**X**) in H_2SO_4–EtOH gives 2' : 4'-*dinitro-4-hydroxy-2 : 3 : 5-trimethylazobenzene* (90%), m.p. 220—221° (decomp.), and with *p*-SO_3H·C_6H_4·NH·NH_2 in aq. EtOH gives a compound, m.p. 224—228° after decomp. Durenol and (**IX**) give 2' : 4'-*dinitro-4-hydroxy-2 : 3 : 5 : 6-tetramethylazobenzene* (95%), orange, m.p. 199—200° (decomp.) (*acetate*, m.p. 181·5—182°), also obtained in a [? polymorphous (*X*-ray)] *form*, deep red, m.p. 197—197·5° (190—191°) (decomp.), from (**VIII**) and (**X**). Reduction of the $(NO_2)_2$-compounds gives inseparable mixtures. The azo-compounds and their acetates are purified by adsorption of impurities on Al_2O_3. R. S. C.

Alkylpyrocatechol esters of phosphorous acid. A. E. Arbuzov and F. G. Valitova (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1940, 529—544).—Esters, RP·OR', where R = *o*-$C_6H_4<\begin{matrix}O\\O\end{matrix}>$ and R' = Me (+*CuBr*, m.p. 130—135°), Et (+*CuBr*, m.p. 142—145°), Pr$^\alpha$ (+*CuI*, m.p. 138°), *Pr*$^\beta$ (+*CuCl*, m.p. 143°; +*CuI*, m.p. 178—179°), Bu$^\alpha$ (+*CuCl*, m.p. 202°), and Bu$^\beta$ (+*CuCl*, m.p. 208—210°) are obtained from RPCl and NaOR' in Et_2O. The esters readily isomerise to RPR'·O, which with H_2O gives RPR'$(OH)_2$ and *o*-OH·C_6H_4·O·P(OH)·R':O. With CH_2PhBr, RP·OR' react as follows: RP·OR' + CH_2PhBr → RPO·CH_2Ph + R'Br. R. T.

Reaction between 2-methylnaphthaquinone and magnesium phenyl bromide. (Miss) H. M. Crawford (*J. Amer. Chem. Soc.*, 1941, **63**, 1070—1073; cf. A., 1940, II, 82; Smith *et al.*, A., 1939, II, 543).—2-Methyl-1 : 4-naphthaquinone and MgPhBr give in poor yield 1 : 4-*dihydroxy*-1 : 2-*diphenyl*-2-, m.p. 189—190° [with $K_2Cr_2O_7$ gives COPhMe and *o*-C_6H_4Bz·CO_2H (**I**)], and -3-*methyl*-1 : 2-*dihydronaphthalene* (**II**), m.p. 196·5—197° (or, in one experiment, a *substance*, m.p. 218—220°). (**II**) is oxidised to (**I**), BzOH, and *substances*, m.p. 243—244° (**III**) and 215—217°, and is dehydrated, best by $ZnCl_2$–HCl–C_6H_6, to 3 : 4-*diphenyl*-2-*methyl*-1-*naphthol* (**IV**), m.p. 181—182° [*acetate* (**V**), m.p. 176—177°, obtained also from (**II**) by Ac_2O]. $K_2Cr_2O_7$–AcOH–H_2O oxidises (**IV**) to 3 : 4-diphenyl-1 : 2-naphthaquinone, but (**V**) gives (**III**). (**II**), (**IV**), and (**V**) have no vitamin-*K* activity in 5-mg. doses, but 2-methyl-1 : 4-naphthaquinone has a potency of 2000 units per mg. R. S. C.

Interactions between polycyclic hydrocarbons and sterols in mixed surface films at the air–water interface.—See A., 1941, I, 257.

Isolation of a new phytosterol, campesterol. E. Fernholz and H. B. MacPhillamy (*J. Amer. Chem. Soc.*, 1941, **63**, 1155—1156).—Rapeseed oil yields brassicasterol (acetate bromide insol. in Et_2O–AcOH) and *campesterol* (**I**), $C_{28}H_{48}O$, m.p. 157—158°, $[\alpha]_D^{23}$ −33° in $CHCl_3$ (*acetate*, m.p. 137—138°, $[\alpha]_D^{23}$ −35° in $CHCl_3$; *benzoate*, m.p. 158—160°, $[\alpha]_D^{23}$ −8·6° in $CHCl_3$; 3 : 5-*dinitrobenzoate*, m.p. 202—203°, $[\alpha]_D^{23}$ −6·0° in $CHCl_3$; absorbs 1 O from BzO_2H; sol. acetate bromide). (**I**) is also obtained from soya-bean oil (by way of the bromide; with stigmasterol) and wheat-germ oil (directly), but not cotton-seed or tall oil. R. S. C.

Constitution of campesterol. E. Fernholz and W. L. Ruigh (*J. Amer. Chem. Soc.*, 1941, **63**, 1157—1159).—Campesterol (**I**) is shown to differ from 22 : 23-dihydrobrassicasterol only in configuration at $C_{(24)}$. Its acetate is hydrogenated (H_2–PtO_2–AcOH; later reacetylation) to *campestanyl acetate* (**II**), m.p. 143—144°, $[\alpha]_D^{23}$ +18·3° in $CHCl_3$, and oxidised (CrO_3–90% AcOH; 95°; later hydrolysis by 2N-NaOH) to β-3-hydroxy-nor*allo*cholanic acid, (?) *d*-Me γδ-dimethylamyl ketone (*semicarbazone*, m.p. 152—153°, $[\alpha]_D^{24}$ +11·9° in $CHCl_3$, does not depress the m.p. of the *l*-isomeride), and $COMe_2$. 5% KOH–EtOH hydrolyses (**II**) to *campestanol*, m.p. 146—147°, $[\alpha]_D^{24}$ +31° in $CHCl_3$ (3 : 5-*dinitrobenzoate*, m.p. 198°, $[\alpha]_D^{24}$ +22° in $CHCl_3$). (**I**) gives *i*-campesteryl *p*-toluenesulphonate, m.p. 150—152°, and thence *i-campesteryl Me ether*, m.p. 61—63°, $[\alpha]_D^{24}$ +62° in $CHCl_3$. R. S. C.

Sterols. CXX. Anterior pituitary gland extracts. R. E. Marker and E. L. Wittbecker (*J. Amer. Chem. Soc.*, 1941, **63**, 1031—1032).—$COMe_2$ extracts from anterior pituitary glands

(ox) cholesterol (only sterol), Na stearate, *substances* (*a*), $C_8H_{10}O_4N_4$ or $C_{10}H_{13}O_5N_5$, m.p. 281—284°, and (*b*) $C_{20}H_{40}O_2$, m.p. 96—98°, a *carbinol*, m.p. 79—81°, and the known hydrocarbon, $C_{28}H_{58}$. R. S. C.

Effect of *ortho*-substitution on bacteriostatic properties of phenylacetic acid. C. F. Feasley and B. H. Gwynn [with E. F. Degering and P. A. Tetrault] (*J. Amer. Pharm. Assoc.*, 1941, **30**, 41—45).—Slow addition of HNO_3 (*d* 1·41) to *p*-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ in boiling AcOH–I yields 2-*iodo*-4-*nitrophenylacetic acid*, m.p. 236°, reduced (H_2, colloidal Pt, EtOH) to 2-*iodo*-4-*aminophenylacetic acid*, m.p. 184°. For bacteriostatic properties of these and related compounds, cf. A., 1941, III, August. F. O. H.

Normal and alkaline esters of *m*-aminomandelic acid and related compounds. L. S. Fosdick and J. C. Calandra (*J. Amer. Chem. Soc.*, 1941, **63**, 1101—1103; cf. A., 1938, II, 322).—Crude *m*-$NO_2{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CN$ (prep. described) with HCl–ROH gives *Me*, m.p. 66°, Et, m.p. 63°, *Pr*$^{\alpha}$, m.p. 73°, *Pr*$^{\beta}$, m.p. 57°, and *Bu*$^{\alpha}$ m-*nitromandelate*, m.p. 65°, hydrogenated (PtO_2; 45 lb.) to the *NH*$_2$-*esters*, m.p. 139°, 55°, 101°, 146°, and 110°, respectively. *Cl*-[CH_2]$_2$ m-*nitromandelate*, m.p. 76°, gives *Cl*-[CH_2]$_2$ m-*aminomandelate*, m.p. 91°, which with $NHEt_2$ at 100° gives NEt_2-[CH_2]$_2$ *m*-aminomandelate, unstable (*hydrochloride*, m.p. 133°). The NH_2-esters have little or no anæsthetic activity. M.p. are corr. R. S. C.

Reaction of anhydrous rare earth bromides with ethyl benzoate.—See A., 1941, I, 278.

Alkamine esters of *p*-fluorobenzoic acid and their salts. L. S. Fosdick and E. E. Campaigne (*J. Amer. Chem. Soc.*, 1941, **63**, 974—975).—*p*-$C_6H_4F{\cdot}CO_2H$ is obtained in 16% yield from *p*-C_6H_4MeF or from *p*-$C_6H_4Br{\cdot}NH_2$ (by way of *p*-C_6H_4BrF and *p*-$C_6H_4F{\cdot}MgBr$) and in 20% yield from NH_2Ph (by way of PhF and *p*-$C_6H_4F{\cdot}COMe$). *Di-ethyl-*, b.p. 136—137°/7 mm. (*hydrochloride*, m.p. 124—126°; *borate*, *B*,5HBO_2), *-propyl-*, b.p. 149—150°/7 mm. (*hydrochloride*, m.p. 115—117°; *borate*, *B*,5HBO_2), *-butyl-aminoethyl*, b.p. 168—169°/7 mm. (*hydrochloride*, m.p. 115—116°; *borate*, *B*,5HBO_2), *di-ethyl-*, b.p. 148—149°/7 mm. (*hydrochloride*, m.p. 122—124°; *borate*, *B*,7HBO_2), *-propyl-*, b.p. 161—161·5°/7 mm. (*hydrochloride*, m.p. 124—126°; *borate*, *B*,6HBO_2), and *-butyl-aminopropyl*, b.p. 175·5—177°/6 mm. (*hydrochloride*, m.p. 100°; *borate*, *B*,6HBO_2), p-*fluorobenzoate* are described; they are efficient, non-toxic, but irritant anæsthetics. R. S. C.

4 : 5-Dinitro-2-methoxybenzoic acid. H. Goldstein and A. Jaquet (*Helv. Chim. Acta*, 1941, **24**, 30—37).—4 : 2 : 1-$NO_2{\cdot}C_6H_3(OMe){\cdot}CO_2H$ (obtained by oxidation of 4 : 1 : 2-$NO_2{\cdot}C_6H_3Me{\cdot}OMe$ with $KMnO_4$) with HNO_3 (*d* 1·52) and conc. H_2SO_4 at 0° gives 4 : 5-*dinitro*-2-*methoxybenzoic acid* (**I**), m.p. 144°, transformed by conc. NH_3 at room temp. into 5-*nitro*-4-*amino*-2-*methoxybenzoic acid* (**II**), m.p. 248° (*Ac* derivative, m.p. 193°), which is converted (diazo-reactions) into 5 : 2 : 1-$NO_2{\cdot}C_6H_3(OMe){\cdot}CO_2H$ and 4-*iodo*-5-*nitro*-2-*methoxybenzoic acid*, m.p. 227°. (**I**) and KOH–MeOH at 50° give 5-*nitro*-2 : 4-*dimethoxybenzoic acid*, m.p. 220° (Me ester, m.p. 150°), reduced ($SnCl_2$–conc. HCl) to 5-*amino*-2 : 4-*dimethoxybenzoic acid*, m.p. 199° (*Ac* derivative, m.p. 217°). (**I**) is transformed by boiling 7% NaOH into 5-*nitro*-4-*hydroxy*-2-*methoxybenzoic acid*, m.p. 192°. When heated with the requisite base, (**I**) is converted into 5-*nitro*-4-*dimethylamino*-, m.p. 208°, 5-*nitro*-4-*anilino*-, m.p. 204°, 5-*nitro*-4-*phenylhydrazino*- (**III**), m.p. 193°, and 5-*nitro*-4-*hydrazino*-, m.p. 237° (*Ac*, m.p. 256°, and *CMe*$_2$, m.p. 242°, derivatives), -2-*methoxybenzoic acid*. (**III**) is transformed by boiling glacial AcOH into 3-*oxido*-6-*methoxy*-2-*phenylbenztriazole*-5-*carboxylic acid*, m.p. 208°. (**I**) is slowly transformed by Na_2S_2 in boiling EtOH into *di*-6-*nitro*-3-*methoxy*-4-*carboxyphenyl disulphide*, m.p. 264° (decomp.). M.p. are corr. H. W.

Chlorination of derivatives of *o*-orsellinic acid. T. J. Nolan and D. Murphy (*Sci. Proc. Roy. Dublin Soc.*, 1941, **22**, 315—319).—Et *o*-orsellinate and Cl_2 in CCl_4 at room temp. give the 4 : 6-Cl_2-derivative (**I**), m.p. 158—161°, hydrolysed (boiling 5% aq. KOH) to 2 : 4-*dichloro-orcinol*, m.p. 121°, converted by CH_2N_2–$COMe_2$ into the Me_2 ether, an oil. Equimol. amounts of Me *o*-orsellinate (**II**) and Cl_2 in $CHCl_3$–CCl_4 at room temp. give *Me* 4 : 6-*dichloro*-o-*orsellinate* (+0·5H_2O) (**III**), m.p. 117°. (**II**) with excess of Cl_2 in $CHCl_3$–CCl_4 at room temp. affords *Me* 3 : 3 : 5 : 5-*tetrachloro*-2 : 4-*diketo*-6-*methyl*-2 : 3 : 4 : 5-*tetrahydrobenzoate*, m.p. 132—134°, converted by $SnCl_2$ in AcOH–HCl at room temp. into (**III**). (**I**) with excess of CH_2N_2 in Et_2O–$COMe_2$, followed by hydrolysis (boiling 5% aq. KOH), gives 4 : 6-*dichloro*-3 : 5-*dimethoxy*-o-*toluic acid*, m.p. 135—136°. Equimol. amounts of *o*-orsellinic acid and CH_2N_2 in Et_2O–$COMe_2$ give Me 3-hydroxy-5-methoxy-*o*-toluate (**IV**), m.p. 63—65°, which with a small excess of Cl_2 in $CHCl_3$–CCl_4 gives *Me* 4 : 6-*dichloro*-3-*hydroxy*-5-*methoxy*-o-*toluate* (**V**), m.p. 79—81°. With excess of Cl_2, (**IV**) gives *Me* 3 : 3 : 5 : 5-*tetrachloro*-2-*keto*-4-*methoxy*-6-*methyl*-2 : 3 : 4 : 5-*tetrahydrobenzoate*, m.p. 144—146°, reduced ($SnCl_2$–AcOH–HCl) to (**V**). J. L. D.

Manufacture of unsaturated aldehydes.—See B., 1941, III, 161.

Reactions of 2 : 8-dihydroxy-I-naphthaldehyde. R. Adams and D. E. Burney (*J. Amer. Chem. Soc.*, 1941, **63**, 1103—1107).—2 : 8 : 1-$(OH)_2C_{10}H_5{\cdot}CHO$ (**I**) [prep. from 2 : 8-$C_{10}H_6(OH)_2$ by $Zn(CN)_2$–HCl in 34—38% yield] and its derivatives do not react in the tautomeric forms characteristic of the gossypol series. (**I**) gives a normal phenylhydrazone and *oxime* (**II**), m.p. 161—162°, dehydrated by Ac_2O at room temp. to 2-*hydroxy*-peri-*naphthoxazine* (**III**), m.p. 190—191°, the *Me ether* (prep. by CH_2N_2–Et_2O or K_2CO_3–Me_2SO_4–$COMe_2$), m.p. 111—112°, of which with boiling Ac_2O–NaOAc gives 8-*acetoxy*-, m.p. 94·5—96°, and thence by HCl 8-*hydroxy*-2-*methoxy*-1-*naphthonitrile* (**IV**), m.p. 194—195°. 10% KOH–MeOH converts (**III**) into (**IV**). The *Ac* derivative, m.p. 159—160°, of (**III**) is obtained by Ac_2O from (**II**) or (**III**) and is converted by boiling Ac_2O–NaOAc into 2-*acetoxy*-peri-*naphthoacetimidolactone*, m.p. 100—101° [also obtained similarly from (**II**) or (**III**)]. Conc. HCl at room temp. then gives 2-*hydroxy*-peri-*naphtholactone* (90%), m.p. 193—194° (*acetate*, m.p. 134—135°), the *Me ether* (prep. by CH_2N_2–Et_2O or K_2CO_3–Me_2SO_4–$COMe_2$), m.p. 128—129°, of which with hot Me_2SO_4–aq. NaOH gives *Me* 2 : 8-*dimethoxy*-1-*naphthoate*, m.p. 131—132°. 2 : 8-*Dimethoxy*-1-*naphthaldehyde* [prep. from (**I**) by Me_2SO_4–K_2CO_3–$COMe_2$], m.p. 90—91° (*phenylhydrazone*, m.p. 126—127°), gives the *oxime*, m.p. 137—139°, dehydrated by boiling Ac_2O to 2 : 8-*dimethoxy*-1-1-*naphthonitrile*, m.p. 148—149°, which is also obtained from (**IV**) by Me_2SO_4–NaOH. M.p. are corr. R. S. C.

Metallic derivatives of acetomesitylene. H. Gilman and R. G. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 1162—1163).—The MgBr derivative of acetomesitylene (**I**), prepared by MgPhBr, gives the Michler's ketone test. The Li and Na derivatives (prep. by LiPh and NaPh, respectively) regenerate 97 and 86%, respectively, of (**I**) and give the Michler's ketone test. R. S. C.

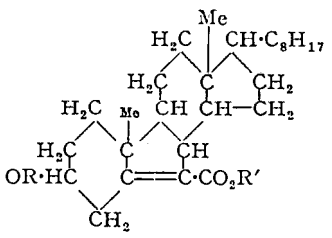
Hydroxyalkyl ethers of substituted acylphenols.—See B., 1941, II, 177.

Naphthalene series. VI. Synthesis of 2-propyl-1-naphthol and properties of 2-propionyl-1-naphthol. VII. Attempted synthesis of 4-stearyl-, 4-palmityl-, and 4-lauryl-1-naphthol. R. D. Desai and W. S. Waravdekar (*Proc. Indian Acad. Sci.*, 1941, **13**, A, 33—38, 39—42).—VI. α-$C_{10}H_7{\cdot}OH$ with hot $EtCO_2H$ and $ZnCl_2$ yields 2-propionyl-1-naphthol (**I**) (*picrate*, m.p. 88°; *semicarbazone*, m.p. 304°; *phenylhydrazone*, m.p. 78°; p-*nitrophenylhydrazone*, m.p. 232°; *Me ether*, m.p. 45°). (**I**) with $AlCl_3$ in $PhNO_2$ at room temp. gives a *compound*, $C_{28}H_{22}O_4$, m.p. >300°, and with Br in AcOH–I (trace) yields 4-bromo-2-propionyl- (**II**) and 4-*bromo*-2-α-*bromopropionyl*-1-*naphthol* (**III**), m.p. 145°. (**II**) with NaOAc and Ac_2O at 180—185° yields 6-bromo-2 : 3-dimethyl-1 : 4-α-naphthapyrone, new m.p. 225°, hydrolysed (10% NaOH) to 1 : 4 : 2-OH·$C_{10}H_5Br{\cdot}CO_2H$. (**III**) with 10% NaOH yields 4-*bromo*-2-*lactyl*-1-*naphthol*, m.p. 214°, and with NaOMe in MeOH affords 4-*bromo*-2-*acrylyl*-1-*naphthol*, m.p. 204°, and 5-*bromo*-2-*methylnaphthacoumaranone*, m.p. 252°. HNO_3 (*d* 1·5; 1 mol.) and (**I**) in AcOH give 4-*nitro*-2-*propionyl*-1-*naphthol*, m.p. 162°, which with NaOAc and Ac_2O at 100—140° yields 6-*nitro*-2 : 3-*dimethyl*-1 : 4-α-*naphthapyrone*, m.p. 226°, hydrolysed (10% NaOH) to 4 : 1 : 2-$NO_2{\cdot}C_{10}H_5(OH){\cdot}CO_2H$; with 2 or >2 mols. of HNO_3, 2 : 4 : 1-$(NO_2)_2C_{10}H_5{\cdot}OH$ is formed. Reduction (Clemmensen) of (**I**) yields 2-*propyl*-1-*naphthol* (**IV**), b.p. 165°/6 mm. (*picrate*, m.p. 113°; *Me ether*, b.p. 145°/6 mm.), and (?) 2-*propyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthol*, b.p. 120—121°/7 mm. (**IV**) with PhN_2Cl yields 4-*benzeneazo*-2-*propyl*-1-*naphthol*, m.p. 180°, and the *phenylhydrazone*, m.p. 112°, of 2-*propyl*-1 : 4-*naphthaquinone*, m.p. 243°.

VII. α-$C_{10}H_7{\cdot}OH$, stearyl chloride, and $ZnCl_2$ in $PhNO_2$ at

room temp. yield 2- (80%) and 4-*stearyl*-1-*naphthol* (6%), m.p. 159—160°. α-$C_{10}H_7$·OMe similarly yields 70% of 1-*methoxy*-4-*stearylnaphthalene*, m.p. 125—126° (with some 4 : 4′-dimethoxy-1 : 1′-dinaphthyl), which with $AlCl_3$ in C_6H_6 gives only $C_{17}H_{35}$·CO_2H and α-$C_{10}H_7$·OH, but is reduced (Clemmensen) to 1-*methoxy*-4-*octadecylnaphthalene*, m.p. 202—203°. Similar methods yield 1-*methoxy*-4-*palmityl*- (which with $AlCl_3$ in C_6H_6 gives only $C_{15}H_{31}$·CO_2H and α-$C_{10}H_7$·OH), -*hexadecyl*-, m.p. 224—225°, -*lauryl*-, m.p. 111—112°, and -*dodecyl*-*naphthalene*, m.p. 165—166°. A. LI.

[Relation between] structure and absorption spectra of αβ-unsaturated ketones. R. B. Woodward (*J. Amer. Chem. Soc.*, 1941, **63**, 1123—1126).—The following corrections convert absorption max. of αβ-unsaturated ketones in the solvent named into max. in abs. EtOH : MeOH −1, $CHCl_3$ 0, Et_2O +6, hexane +7 mμ. Structure and the position of absorption max. are strictly correlated as follows: CO·CH:CHR or CO·CR:CH_2 225±5, CO·CH:CRR′ or CO·CR:CHR′ 239±5, CO·CR:CR′R″ 254±5 mμ. It is suggested that the substances (absorption max. <230 mμ.) obtained (Heilbron *et al.*, A., 1938, II, 103) from halogeno-6-ketocholestanyl acetates by basic reagents have the annexed structure.



R. S. C.

Colour reaction for phenolic steroids (naturally occurring œstrogens). I. S. Kleiner (*J. Biol. Chem.*, 1941, **138**, 783—784).—Œstrone (I), œstriol, and œstradiol with *o*-$C_6H_4(CO)_2O$ and $SnCl_4$ at 116—120° yield characteristic phthalein colours not given by non-phenolic steroids. Quant. results may be obtained with as little as 0·25 μg. of (I). A. LI.

Absorption spectra in relation to quinones : 1 : 4-naphthaquinone, anthraquinone, and their derivatives.—See A., 1941, I, 238.

1-Alkylamino-4-hydroxyanthraquinones.—See B., 1941, II, 179.

III.—TERPENES.

Detection and estimation of α-terpinene by means of the diene synthesis. R. M. Gascoigne (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 353—358).—Combination (modified method of Birch, B., 1938, 981) of α-terpinene (I) (purified by method of Richter *et al.*, A., 1930, 1172) and maleic anhydride (II) to the adduct, m.p. 60—61°, is quant. at room temp.; 94% purity of (I) was shown by this method. (I) regenerated from its dihydrochloride is absorbed to the extent of 44% by (II). The product from α-terpineol and dil. H_2SO_4 on reacting with (II) (modified method of Diels *et al.*, A., 1938, II, 330) gives a 52% content of (I). (I) and *p*-O:C_6H_4:O in EtOH afford *α-terpinene–benzoquinone adduct*, m.p. 87—88°, in 29% yield. A. T. P.

Configuration of the nickel salt of formylcamphor.—See A., 1941, I, 238.

Fission of the *cyclo*propane ring of α-thujene. R. M. Gascoigne (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 359—364).—α-Thujene (I) (from *Eucalyptus dives* oil), b.p. 152—153°/760 mm., $[\alpha]_D^{21}$ +19·61°, and warm 5% HCl–EtOH afford α- (II) and γ-terpinene (III) (does not react with maleic anhydride). Probably (I) changes into (III), which partly isomerises to (II). (I) heated with maleic anhydride yields the α-terpinene adduct, the *dl*-α-phellandrene adduct, and *p*-cymene; any (III) formed would be immediately isomerised. (I) and *p*-O:C_6H_4:O in HCl–EtOH afford the α-terpinene–*p*-benzoquinone adduct. A. T. P.

Volatile vegetable substances. XIII. α- and β-Vetivone. Y. R. Naves and E. Perrottet (*Helv. Chim. Acta*, 1941, **24**, 3—29).—α- (I) and β-Vetivone (II) are steric isomerides and their mol. structure should be interpreted on an approx. tetrahedral basis modified by constraint due to cyclisation and to space relationships. (I) (2 : 4-*dinitrophenylhydrazone*, m.p. 149°) purified through its semicarbazone, m.p. 222—223°, $[\alpha]_D$ +334·20°±0·40° in AcOH, has b.p. 126—127°/0·85 mm., 144—144·5°/2·0 mm., m.p. 51—51·5°, $[\alpha]_D$ +238·25° in EtOH; it rapidly alters on exposure to air. (II) (2 : 4-*dinitrophenylhydrazone*, m.p. 190·5—191°), similarly purified through the semicarbazone, m.p. 228—229°, $[\alpha]_D$ −71·10° in AcOH, has b.p. 130—132°/1·15 mm., 141—142°/2 mm., m.p. 44—44·5°, $[\alpha]_D$ −38·92° in EtOH. Various colour reactions of (I) and (II) are recorded. Dehydrogenation of (I) by Se at 260—280° and then at 280—300° affords vetivazulene (2·3%; picrate, m.p. 122—122·5°), eudalinol, m.p. 85—85·5° (phenylurethane, m.p. 135°), and a non-azulenic neutral fraction which does not give a well-defined picrate or styphnate. Ozonolysis of (I) gives 1 mol. of $COMe_2$ and smaller proportions of CH_2O and HCO_2H; with (II) the results are similar but the amounts of CH_2O and HCO_2H are less. The *sesquiterpenes* [(III) and (IV)] derived from the semicarbazones of (I) and (II) (Wolff–Kishner) have b.p. 124°/4·2 mm., α_D +98·64°, and b.p. 103—103·5°/2·8 mm., α_D −33·76°; (III) gives an intense blue colour becoming olive-green with Br–$CHCl_3$ whereas (IV) decolorises the reagent. Hydrogenation (PtO_2 in AcOH at 70°) of (III) affords *α-vetivane*, b.p. 102—103°/2·2 mm., α_D −3·21°, whilst (IV) yields *β-vetivane* (V), b.p. 101—102°/2·3 mm., α_D −2·96°; neither gives a colour with Br–$CHCl_3$, or $C(NO_2)_4$. Similar hydrogenation of (I) and (II) gives closely related products, b.p. 106°/2·4 mm., α_D −3·92° and b.p. 94—94·5°/1·65 mm., α_D −1·85°, very like the decahydro-S- and -Se-guaiazulene of Ruzicka and Haagen-Smit. The attempted isomerisation of (V) by $AlCl_3$ gives a hydrocarbon, $C_{15}H_{28}$, b.p. 98—99°/3·2 mm., α_D ±0° which is scarcely affected by Se at 280—300°. The alcoholic fraction obtained by the hydrogenation of (II) contains *tetrahydro-β-vetivol* [*β-vetivanol*] (VI), m.p. 108—108·5°, $[\alpha]_D$ 0° in EtOH (3 : 5-*dinitrobenzoate*, m.p. 161—161·5°; *allophanate*, m.p. 196—196·5°; the *allophanate* of the isomeric β-vetivanol, m.p. 76—76·5°, has m.p. 218—218·5°). (VI) is oxidised (CrO_3 in AcOH) to *tetrahydro-β-vetivone* [*β-vetivanone*], b.p. 134—136°/2 mm., m.p. 38° (*semicarbazone*, m.p. 198·5—199°). Partial hydrogenation (Raney Ni; EtOH) of (II) gives 6 : 7-dihydro-β-vetivol, m.p. 108·5—109°, α_D ±0° (3 : 5-dinitrobenzoate, m.p. 129·5—130°; *allophanate*, m.p. 221—221·5°). *Tetrahydro-α-vetivol* [*α-vetivanol*], b.p. 132·5—134°/2·5 mm., α_D ±0° (*allophanate*, m.p. 225·5—226°; non-cryst. 3 : 5-dinitrobenzoate), obtained by hydrogenation of (I), is oxidised to *tetrahydro-α-vetivone* [*α-vetivanone*] (*semicarbazone*, m.p. 224·5—225°; isomeric 2 : 4-*dinitrophenylhydrazones*, m.p. 95—95·5° and 131·5—132°, respectively). H. W.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Sterols. CXV. Sapogenins. XLIV. Relation between diosgenin and cholesterol. R. E. Marker and D. L. Turner (*J. Amer. Chem. Soc.*, 1941, **63**, 767—771).—Diosgenin (I) and Zn–Hg in conc. HCl–EtOH give *tetrahydrodiosgenin* (II), m.p. 178—179° [*triacetate* (III), m.p. 119·5°; *tribenzoate*, m.p. 166—167°], whence H_2–PtO_2 at 3 atm. in AcOH yields *tetrahydrotigogenin*, m.p. 195—197° [*triacetate*, m.p. 67—68°, also obtained by similar hydrogenation of (III); *tribenzoate*, m.p. 162°]. SeO_2 in boiling 97% AcOH, followed by KOAc, and finally EtOH–KOH, oxidises (III) to a *tetrahydroxycholestene*, m.p. 196°, converted by boiling HCl–EtOH into 16 : 27-*dihydroxy*-3-*keto*-Δ^4-*cholestene*, m.p. 163—164°. Treatment of (II) with PBr_3 in boiling C_6H_6, then with KOAc–AcOH, and finally with Na–PrOH gives Δ^5-cholestene (reduced catalytically to cholestane) and cholesterol. Diosgenin acetate and CrO_3 in AcOH at 50—53° give an *acid*, $C_{27}H_{40}O_5$, decomp. 226° (rapid heating to 200°), 7-*ketodiosgenin acetate* (IV), m.p. 197°, and unchanged material. NaOEt–EtOH at 180° converts the *semicarbazone*, decomp. 282°, of (IV) into (V) (below) (small yield). With boiling 15% KOH–EtOH, (IV) gives (?) 7-*keto*-3 : 5-*dihydrotigogenin*, $C_{27}H_{38}O_3$, m.p. 197—198°. 4-Dehydrotigogenone with Zn–Hg–HCl–EtOH or Zn–HCl–EtOH gives 4-*dehydrodeoxytigogenin*, m.p. 145·5—146°, and with $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ gives 3 : 5-*dehydrodeoxytigogenin* (V), m.p. 168—169°, reduced (H_2–Pd–$BaSO_4$–Et_2O) to deoxytigogenin. Treating (I) with *p*-O:C_6H_4:O in PhMe and then with $Al(OPr^{\beta})_3$ gives, after removal of acids and carbinols, 4 : 6-*dehydrotigogenone*, m.p. 205—207°. Chlorination of (I) gives *chlorodeoxydiosgenin*, m.p. 211—213°, hydrogenated (PtO_2; AcOH) to 3-*chlorodeoxytigogenin* (VI), m.p. 204—207°. An *isomeride*, m.p. 210—212°, of (VI) is obtained from tigogenin by PCl_5 and $CaCO_3$ in $CHCl_3$ at 20° and in boiling quinoline

gives 2-*dehydrodeoxytigogenin*, m.p. 163—166°. 4-Dehydrotigogenone and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give 4-*dehydroepitigogenin*, m.p. 208—210° [in boiling Ac_2O gives (?) (V)], and a *product*, m.p. 167—169° (digitonide; dehydrated at 100°/vac.).

R. S. C.

Sterols. CXXI. Sapogenins. XLVIII. Bromosarsasapogenin and bromodiosgenin. R. E. Marker, D. L. Turner, A. C. Shabica, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1941, **63**, 1032—1034).—The Br of bromosarsapogenin (I) is shown to be at $C_{(23)}$. The acetate of (I) and CrO_3 at 60° give 3-hydroxy-16-ketobisnorcholanic acid. Diosgenin acetate (II), Br, and a drop of HBr in AcOH at 20° give the 5 : 6 : 23-Br_3-derivative (III), m.p. 172° (decomp.), converted by KI in boiling EtOH into 23-*bromodiosgenin acetate*, m.p. 177—179° (decomp.) or 197—198° (decomp.), which is reduced by Zn–AcOH to (II), is hydrolysed by boiling 1% KOH–EtOH to *bromodiosgenin*, m.p. 195° (decomp.), is oxidised by SeO_2 (with subsequent hydrolysis) to 23-*bromo*-4-*hydroxydiosgenin*, m.p. 203° (decomp.), and with CrO_3–AcOH–H_2O at 50° gives (?) 7 : 16-*diketo*-3-*acetoxy*-Δ^5-*bisnorcholenic acid*, m.p. 226—227° (*semicarbazone*, decomp. 195°), and a small amount of 23-*bromo*-7-*ketodiosgenin acetate*, decomp. 214°. With 1% EtOH–KOH followed by CrO_3–AcOH at 20° and then KI–EtOH, (III) gives 23-*bromo*-4-*dehydrotigogenone*, decomp. 214°.

R. S. C.

Sterols. CXVI. Sapogenins. XLV. *iso*Sarsasapogenin configuration. R. E. Marker, D. L. Turner, R. B. Wagner, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1941, **63**, 772—774).—Reactions are described supporting the view that sapogenins having the *iso*sarsasapogenin differ from those having the sarsasapogenin configuration only in configuration at $C_{(22)}$. Tigogenin and $H_2S_2O_8$–AcOH at 25° give allo*pregnane*-3(β) : 16 : 20-*triol*, m.p. 235—237° (*triacetate*, m.p. 166°; *tribenzoate*, m.p. 204°), also obtained from tigogenin acetate by 30% H_2O_2 in AcOH at 70° and later KOH–EtOH. *epi*-Tigogenin gives $(H_2S_2O_8)$ allo*pregnane*-3(α) : 16 : 20-*triol*, m.p. 210—212° (*triacetate*, m.p. 148—150°), whilst smilagenin affords the same pregnane-3(β) : 16 : 20-triol, m.p. 223—226°, as is obtained (A., 1940, II, 376) from sarsasapogenin. Diosgenin and MgEtBr in Et_2O, later boiling C_6H_6, give 22-*ethyldihydrodiosgenin*, m.p. 211—214° (*di*-p-*nitrobenzoate*, m.p. 183—184°), hydrogenated (PtO_2–AcOH; 35 lb.) to 22-*ethyldihydrotigogenin*, m.p. 192—194° (*di*-p-*nitrobenzoate*, m.p. 183—184°), which is obtained also from tigogenin by MgEtBr and with CrO_3 in 90% AcOH at 15° gives the *keto-acid*, $C_{29}H_{46}O_4$, m.p. 221—223°. Smilagenin and MgEtBr give a 22-*ethyldihydro*-derivative, m.p. 161—162° (*diacetate*, m.p. 89—91°), isomeric with that obtained from sarsasapogenin.

R. S. C.

V.—HETEROCYCLIC.

Co-ordination compounds with furfuraldoxime as a chelate group. I. Additive compounds with metallic salts. A. Bryson and F. P. Dwyer (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 107—109).—β-Furfuraldoxime and $CuCl_2,2H_2O$–EtOH, Cu_2Cl_2–EtOH, $AgNO_3$–aq. EtOH, aq. $AgClO_4$, Ag_2SO_4–aq. EtOH, $NiCl_2,6H_2O$–EtOH, or $CoCl_2,6H_2O$–EtOH, respectively, afford *compounds*, $Cu(C_5H_5O_2N)_2Cl_2$, $Cu(C_5H_5O_2N)_2Cl$, $Ag(C_5H_5O_2N)_2NO_3$, $Ag(C_5H_5O_2N)_2ClO_4$, $Ag_2(C_5H_5O_2N)_4SO_4$, $Ni(C_5H_5O_2N)_4Cl_2$, and $Co(C_5H_5O_2N)_4Cl_2$, respectively. α-Furfuraldoxime does not give additive compounds with metallic salts, but rearranges to give an additive compound of the β-oxime.

A. T. P.

Furfuraldoxime as a chelate group. II. Palladium compounds with α-(*syn*)furfuraldoxime. A. Bryson and F. P. Dwyer (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 240—246).—Pd alone of the common metals forms complexes with α-furfuraldoxime (I) (cf. A., 1935, 752, and *J. Proc. Roy. Soc. N.S. Wales*, 1935, **68**, 107). (I) and Na chloropalladite in aq. EtOH–NaOAc afford *Pd bis-α-furfuraldoxime* (II), $Pd(C_5H_4O_2N)_2$ (*monomeric* form), decomp. without melting; keeping the solid or a conc. solution in $COMe_2$, at room temp. converts it into the trimeric *form* (III), $[Pd(C_5H_4O_2N)_2]_3$, decomp. without melting. (I) can be recovered from either form. Structural formulæ are given. (II) in cold C_5H_5N yields *bispyridine palladous oximate* (IV), $Pd(C_5H_4O_2N)_2,2C_5H_5N$ (C_5H_5N is lost at 100—110°), converted by cold dil. HCl into $Pd(C_5H_5N)_2Cl_2$. (IV) is sol. in H_2O or $CHCl_3$, indicating an equilibrium between the true ionic oximate form and a covalent form. In boiling $CHCl_3$ with C_5H_5N or *p*-$C_6H_4Me{\cdot}NH_2$, (III) shows no evidence of further co-ordination. (III) and C_5H_5N at 80—90° give *bispyridine Pd bisfurfuraldoxime*, $[Pd(C_5H_4O_2N)_2]_3,2C_5H_5N$, gradually decomp. in C_5H_5N at 90° to give (IV). (II) or (III) and $(CH_2{\cdot}NH_2)_2$–C_6H_6–$CHCl_3$ afford the same *ethylenediamine compound* (V), $Pd(C_5H_4O_2N)_2,C_2H_8N_2$, sol. in H_2O or $CHCl_3$, and considered to be ethylenediamine palladous oximate in equilibrium with ethylenediamine Pd bisfurfuraldoxime. (V) and $(CH_2{\cdot}NH_2)_2$–$CHCl_3$ give the ionic H_2O-sol. bisethylenediamine *compound*.

A. T. P.

2-Hydroxy-4-benzoyl-2 : 5-diphenylfuran-3-one. R. E. Lutz, J. M. Smith, jun., and A. H. Stuart (*J. Amer. Chem. Soc.*, 1941, **63**, 1143—1148).—COPh·CO·CH:CPh·ONa and BzCl in boiling Pr^{β}_2O give benzoates [including COPh·CH:C(OBz)·COPh and (?) COPh·CO·CH:CPh·OBz], whence 10% NaOH–aq. MeOH yields 2-hydroxy-4-benzoyl-2 : 5-diphenyl-2 : 3-dihydrofuran-3-one (I) (15%), m.p. 166° (cf. A., 1936, 1524). Reactions below are considered to prove that (I) has only the furan structure; alternative nechanisms are set out for those reactions which appear to indicate existence of (I) in open-chain phase. Kurt-Meyer titration with Br–EtOH at −16° to −19° is too slow for an enol (56—60% in 1, 74% in 5, 99% in 120 sec.). Boiling HCl–80% EtOH has no effect on (I), which is also remarkably stable to alkali. Hydrolysis requires boiling 33% KOH in 50% MeOH, yielding then a substance (*semicarbazone*, m.p. 285°), BzOH, and $(CHO)_2$. The *benzoate* (II), m.p. 182°, of (I) was isolated in poor yield as intermediate in the prep. of (I) and was also obtained (~80%) from (I) by Bz_2O–H_2SO_4 at room temp. (not by BzCl) or (20%) from the Ag salt of (I) by BzCl in boiling Pr^{β}_2O. Ac_2O and a drop of H_2SO_4 convert (I) at 25° into its *acetate*, m.p. 120·5°, which in 10% KOH–MeOH–H_2O at 60° regenerates (I). With HCl–MeOH at room temp., (I) or (II) gives 4-*benzoyl*-2-*methoxy*-2 : 5-*diphenyl*-2 : 3-*dihydrofuran*-3-*one* (III), m.p. 131°, also obtained (15%) from the Ag salt of (I) and MeI in boiling Pr^{β}_2O and converted by *o*-$C_6H_4(NH_2)_2$ into 2-*phenyl*-3-*dibenzoylmethylquinoxaline* (V), m.p. 157° (cf. below), and by O_3 in $CHCl_3$ into BzOH (37%; no $BzCO_2H$ is isolated). 4-*Benzoyl*-2-*ethoxy*-2 : 5-*diphenyl*-2 : 3-*dihydrofuran*-3-*one*, m.p. 83°, is similarly obtained from (II) by HCl–EtOH. Boiling (I) in $SOCl_2$ gives, probably, the 2-Cl-compound, since the oily product is converted by NaOMe–MeOH at 0° into (III). Br and (I) in EtOH at 0° give β-*bromo*-β-*benzoyl*-$\alpha\delta$-*diphenylbutan*-$\alpha\gamma\delta$-*trione* (V), m.p. 114·5°, which with KI regenerates (I) and with HCl–MeOH gives (III) and a small amount of a product, m.p. 110°. (IV) is obtained slowly at the b.p. from (I) in EtOH but immediately from (V) or (VI) (see below); it gives a slowly deepening $FeCl_3$ colour and with NaOMe gives an unstable enolic form, m.p. 60—65°, which gives an immediate deep $FeCl_3$ colour; with boiling NH_2OH– or $NHPh{\cdot}NH_2$–NaOAc or a little HCl in boiling 75% EtOH, (IV) gives 2-phenyl-3-phenacylquinoxaline, m.p. 166° (cf. *loc. cit.*); with CrO_3–AcOH it gives 2-hydroxy- and 2-carboxy-3-phenylquinoxaline and BzOH. CH_2N_2–Et_2O and (I) give OMe·CPh:C(COPh)·CO·COPh (VI), an oil, the structure of which is proved by the following reactions. At 25° (VI) readily gives (IV); with O_3 in $CHCl_3$ at 0° it gives BzOH, $BzCO_2H$, and MeOBz; with boiling HCl–AcOH or 2% KOH in boiling 70% MeOH it gives (I) (50%); with MeOH–HCl it gives (III); with NaOMe at 25° it gives a substance, m.p. 119—121°. M.p. are corr.

R. S. C.

Synthesis of 2-hydroxy-4-benzoyl-2 : 5-diphenylfuran-3-one by way of benzoyldiphenylfuran and bromotribenzoylethylene. R. E. Lutz and J. M. Smith, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 1148—1150).—The structure of 2-hydroxy-4-benzoyl-2 : 5-diphenyl-2 : 3-dihydrofuran-3-one (I) is confirmed by a synthesis proving attachment of the Bz to C. $CH_2Bz{\cdot}CHBrBz$ [best prepared from $(CHBz:)_2$ by HBr–AcOH] and H_2SO_4–Ac_2O give 3-bromo-2 : 5-diphenylfuran, the Grignard reagent from which with CO_2 gives 2 : 5-diphenyl-3-furoic acid and with (best) Bz_2O–Et_2O at 0° (later room temp.) gives 3-benzoyl-2 : 5-diphenylfuran (II), m.p. 77° (oxime, m.p. 173—176°; *semicarbazone*, m.p. 225°) (and in both cases also some bis-2 : 5-diphenyl-3-furyl). With Br–CCl_4 or PBr_5 at 25° [not by the method of Kohler *et al.* (A., 1919, i, 533)], (II) gives the 4-Br-derivative, m.p. 119·5—120°, which with HNO_3–AcOH at 50° gives β-*bromo*-γ-*benzoyl*-$\alpha\delta$-*diphenyl*-Δ^{β}-*butene*-$\alpha\delta$-*dione* [*bromotribenzoylethylene*] (54%), m.p. 101°. This is converted by H_2–Pd–$BaSO_4$ into (II), by Zn dust in AcOH at 25° or 50° into a substance (poor yield), m.p. 167—169°, by HCl–MeOH at room temp. into 2-methoxy-4-benzoyl-2 : 5-diphenyl-2 : 3-dihydrofuran-3-one [hydrolysed to (I)], by H_2SO_4–Ac_2O into

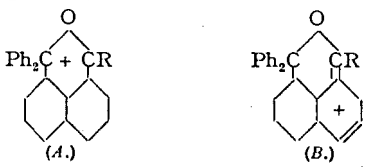
2-acetoxy-4-benzoyl-2 : 5-diphenyl-2 : 3-dihydrofuran-3-one [and thence (I)], by 2% KOH in boiling MeOH into CHBz:CBz·OH, by NaOMe–MeOH at 25° into CHBz:CBz·OMe, and by NH_3–MeOH at room temp. into CHBz:CBz·NH_2. M.p. are corr. R. S. C.

Derivatives of coumaran. VII. Synthesis of *iso*tubanol and *iso*tubaic acid. R. L. Shriner and M. Witte (*J. Amer. Chem. Soc.*, 1941, **63**, 1108—1110; cf. A., 1940, II, 20).—3-Hydroxy-2-keto-1 : 2-dihydrobenzfuran, $COMe_2$, and KOH in abs. EtOH at room temp. give the 1-CMe_2: derivative, m.p. 121° (*phenylurethane*, m.p. 143°), converted by BzCl–Na_2CO_3–aq. $COMe_2$ into 2-*keto*-1-*benzoyloxy*-1-iso*propylidene*-1 : 2-*dihydrobenzfuran*, m.p. 160°. H_2–PtO_2 in abs. EtOH containing a little HCl at 48 lb. then gives 2-hydroxy-3-benzoyloxy-1-*iso*propyl-1 : 2-dihydrobenzfuran, an oil, dehydrated to *iso*tubanol benzoate by distillation. Hydrolysis thereof by NaOH gives *iso*tubanol (*phenylurethane*, m.p. 142°), which with NaOMe–MeOH–CO_2 gives *iso*tubaic acid (acetate, new m.p. 153°; prep. from rotenone by way of *iso*rotenone modified). R. S. C.

Reaction between quinones and metal enolates. XIII. Trimethylethylbenzoquinone and sodiomalonic ester. XIV. Synthesis of the three 6-hydroxy-3-carboxy-*Bz*-dimethylethyl-coumarins and their ethyl esters. L. I. Smith and J. W. Opie (*J. Amer. Chem. Soc.*, 1941, **63**, 932—936, 937—940; cf. A., 1941, II, 144).—XIII. The success and direction of condensation of methyl-*p*-benzoquinones with $CHNa(CO_2Et)_2$ (I) depend on the nature of other substituents. Whereas the Br of 1 : 2 : 3 : 5 : 6 : 4-O:C_6Me_2Br·O causes unidirectional reaction (*loc. cit.*), replacement of the Br by Et gives a much less marked effect. 1 : 2 : 3 : 5 : 6 : 4-O:C_6Et_4:O [prepared from 1 : 2 : 4 : 5-$C_6H_2Et_4$ by way of the $(NO_2)_2$-, m.p. 149—151° (lit. 143—145°), and $(NH_2)_2$-compound], m.p. 60—62° (lit. 56—58°), does not condense with (I). 1 : 2 : 3 : 5 : 6 : 4-O:C_6Me_2Et:O (similar prep. improved), m.p. 43—45°, with (I) in boiling C_6H_6 gives 40% of the derived *quinol*, m.p. 169—170° (*diacetate*, m.p. 136—136·5°), and a red Na salt, hydrolysed to a mixture, whence adsorption on Al_2O_3, fractional elution, and crystallisation gives material, m.p. 185°, shown by thermal analysis to be a binary mixture of *Et* 6-*hydroxy*-7 : 8-*dimethyl*-5-*ethyl*- (II) and 6-*hydroxy*-5 : 8-*dimethyl*-7-*ethyl*-*coumarin*-3-*carboxylate* (III), and material, m.p. 150—152°, shown similarly to be a ternary mixture of (II), (III), and *Et* 6-*hydroxy*-5 : 7-*dimethyl*-8-*ethylcoumarin*-3-*carboxylate* (IV).

XIV. Ethyl-*o*-, -*m*-, and -*p*-xyloquinone, respectively, with Zn–AcOH–H_2O give 2 : 3-*dimethyl*-5-, m.p. 160—160·5°, 2 : 6-*dimethyl*-3-, m.p. 158—158·5°, and 2 : 5-*dimethyl*-3-*ethyl*-*quinol*, m.p. 158—159°, the *diacetates*, m.p. 90—91°, (V) 65—66°, and 74·5—75·5°, of which with Me_2SO_4–KOH–MeOH give the oily Me_2 ethers. With CH_2O–HCl–H_2 these give 2 : 5-*dimethoxy*-3 : 4-*dimethyl*-6-, m.p. 61—62°, -4 : 6-*dimethyl*-3-, m.p. 60—62°, and -3 : 6-*dimethyl*-4-, m.p. 81—82°, *-ethylbenzyl chloride*, which with boiling KOAc–AcOH give the corresponding *acetates*, m.p. 30—40°, an oil, and m.p. 54·5—56·5°, respectively, and thence by KOH–aq. EtOH the *alcohols*, m.p. 116·5—118°, 107—108°, and 127·5—128·5°, respectively. CrO_3–AcOH at <50° then gives 2 : 5-*dimethoxy*-3 : 4-*dimethyl*-6-, m.p. 53—54°, -4 : 6-dimethyl-3-, an oil, and -3 : 6-dimethyl-4-, an oil, -ethylbenzaldehyde, which with (I) in EtOH at room temp. and later boiling 48% HBr give 6-*hydroxy*-7 : 8-*dimethyl*-5-, m.p. 223—224° [Et ester (II), m.p. 180°], -5 : 7-*dimethyl*-8-, m.p. 232—234° [Et ester (IV), m.p. 173—174·5°], and -5 : 8-*dimethyl*-7-, m.p. 250° [Et ester, (III), m.p. 199—201°], *-ethylcoumarin*-3-*carboxylic acid*. CH_2O–HCl converts (V) into 2-*hydroxy*-5-*acetoxy*-4 : 6-*dimethyl*-3-*ethylbenzyl chloride*, m.p. 144·5—146°, which with Na and $CH_2(CO_2Et)_2$ in boiling Et_2O gives *Et* 6-*acetoxy*-5 : 7-*dimethyl*-8-*ethyl*-3 : 4-*dihydrocoumarin*-3-*carboxylate*, m.p. 128·5—129·5°. The corresponding Me_3 compound could not be dehydrogenated. R. S. C.

Reaction between lactones and Grignard reagents. I. Diphenyl-1 : 8-naphthalide. T. A. Geissman and L. Morris (*J. Amer. Chem. Soc.*, 1941, **63**, 1111—1114).—Only 1 mol. of MgRHal reacts with diphenyl-1 : 8-naphthalide (I) to give 1 : 8-$C_{10}H_6<^{CPh_2}_{CR(OH)}>O$. Thus are obtained 1-iso*butyryl*- (II), m.p. 176°, *-propionyl*- (III), m.p. 142—143°, -n-*valeryl*- (IV), m.p. 114—115°, -iso*valeryl*-, m.p. 135—136° (decomp.), and -benzoyl- (V), m.p. (+C_6H_6) ~115° (decomp.), (anhyd.) 200—201° (lit. 202°), -8-α-hydroxybenzhydrylnaphthalene semiketal. In H_2SO_4 the primary alkyl ketones give deep yellow colours and with HCl–AcOH–$FeCl_3$ (III), (IV), and (V) give *ferrichlorides*, m.p. 150—153° (decomp.), 134—135° (decomp.), and 148—150° (decomp.), respectively; the structures (*A*) and (*B*) are assigned to the cations. The semiketals decompose at or slightly > the m.p., yielding (I) and [from (II)] the paraffin (C_3H_8) or [from (III)] the olefine (C_2H_4) and H_2. With NaOAc in boiling AcOH, (III) and (II) give 1 : 1-*diphenyl*-3-*ethylidene*-, m.p. 134°, and *-propylidene*-peri-*naphthopyran*, 1 : 8-$C_{10}H_6<^{CPh_2}_{C(:CRR')}>O$, m.p. 190—194°, respectively.



R. S. C.

Effect of unsaturated chromophores on pyronine dyes. II. Dyes obtained from maleic and succinic acids. I. N. D. Dass and J. D. Tewari (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 68—76; cf. A., 1931, 1426).—Condensation of maleic and succinic acids with 1 : 2 : 3-$C_6H_3(OH)_3$, *o*- and *m*-cresol, and *m*-NH_2·C_6H_4·OH in presence of H_2SO_4 yields *maleins*, m.p. ≮300°, 228°, 155°, and 225° (changing colour at 212°), and *succineins*, m.p. 290°, 230° (blackening at 195°), 112°, and 198° (changing colour at 120°), respectively. *Pyrocatechol-malein*, m.p. 148°, and *-succinein*, m.p. 290°, are prepared without condensing agent and purified by $SnCl_4$. *Phenolmalein* (H_2SO_4) has m.p. 195° (blackening at 170°), *β-naphtholmalein* ($ZnCl_2$), 140° (softening at 133°), *α-naphtholsuccinein* (H_2SO_4), 185°, and m-*phenylenediamine-malein* and *-succinein*, 285° and 210° (changing colour at 192°) respectively. Except those from *m*-NH_2·C_6H_4·OH, the maleins are more coloured than the succineins. *m*-$C_6H_4(OH)_2$ with CO_2H·CH_2·CHBr·CO_2H gives a product (I) similar to resorcinolmalein (II), and with $(CO_2H·CHBr)_2$ yields an acetylenic compound (III) (darkens at 250°, then decomp.). Bromination of (II) or (I) and of (III) yields Br_4-compounds, m.p. 185° and 220° (contracting at 183°) respectively. Dyes of this series crystallise with $1H_2O$. Absorption max. of these compounds are given. A. Li.

Benzopyrone series. III. Synthesis of coumarino- and flavono-α-methyl-7 : 8-dihydrofurans. B. Krishnaswamy and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 43—48).—Umbelliferone with CH_2:CH·CH_2Br and K_2CO_3 in $COMe_2$ yields 7-*allyloxy*-, m.p. 79—80°, transformed by heating at 195—200°/20 mm. into 7-*hydroxy*-8-*allyl*-*coumarin*, m.p. 162—163°. This with $HgCl_2$ in EtOH yields 2'-*chloromercurimethyl*-, m.p. 233—235°, which with I in KI gives 2'-*iodomethyl*-, m.p. 168—169°, reduced (Na + EtOH) to 2'-*methyl*-2' : 3'-*dihydrocoumarino*-(7 : 8-5' : 4')-*furan*, m.p. 148—149°. By similar reactions 7-allyloxy-4-methylcoumarin yields 4-methyl-8-allylumbelliferone, 4-*methyl*-2'-*chloromercurimethyl*-, m.p. 225—227°, and -2'-*iodomethyl*-, m.p. 158—159°, and 2 : 4-*dimethyl*-2' : 3'-*dihydrocoumarino*-(7 : 8-5' : 4')-*furan*, m.p. 182—183°, and 3-*methoxy*-7-*allyloxy*-, m.p. 107—108°, yields 7-*hydroxy*-3-*methoxy*-8-*allyl*-*flavone*, m.p. 243—244°, 3-*methoxy*-2'-*chloromercurimethyl*-, decomp. ~200°, -2'-*iodomethyl*-, m.p. 205—206°, and -2'-*methyl*-2' : 3'-*dihydroflavono*-(7 : 8-5' : 4')-*furan*, m.p. 133—134°. A. Li.

Hæmorrhagic sweet clover disease. V. Identification and synthesis of the hæmorrhagic agent. M. A. Stahmann, C. F. Huebner, and K. P. Link. **VI. Synthesis of the δ-diketone derived from the hæmorrhagic agent through alkaline degradation.** C. F. Huebner and K. P. Link (*J. Biol. Chem.*, 1941, **138**, 513—527, 529—534).—V. A method of mass isolation of the compound $C_{19}H_{12}O_6$ (I), m.p. 288—289° (Campbell *et al.*, A., 1941, III, 23) [*diacetate*, m.p. 250—252° (decomp.)], is described. (I) yields, with KOH at 300°, *o*-OH·C_6H_4·CO_2H, with 30% EtOH–KOH or 10% aq. NaOH, *αγ-disalicoylpropane* (II), m.p. 101—102° (*Me*$_2$ *ether*, m.p. 86—88°) (which, fused with KOH, gives *o*-OH·C_6H_4·CO_2H), with NH_2Ph at 180°, 4-anilo-3 : 4-dihydrocoumarin, m.p. 262—263°, and with NHPh·NH_2, a *diphenylhydrazone*, $C_{21}H_{10}O_2N_4$, m.p. 189—189·5°. (I) is 3 : 3'-methylenebis-(4-hydroxycoumarinyl) (Anschütz, A., 1909, i, 663) (from 4-hydroxycoumarin and CH_2O), which shows hæmorrhagic activity in rabbits.

VI. (II) with N_2H_4,HCl and NaOAc yields a *compound*, $C_{17}H_{16}O_2N_2$, m.p. 252°, which gives a yellow colour with aq. NH_3. *o*-OMe·C_6H_4·CO·CH_2·CO_2Et (from *o*-OMe·C_6H_4·CO_2Me and EtOAc), new m.p. 130—131°, with Na and CH_2I_2 in C_6H_6 yields a product hydrolysed (cold 10% NaOH) to the *Me*$_2$ *ether*, m.p. 86—88, of (II). Ph glutarate with $AlCl_3$ in CS_2 yields (II). A. Li.

Isosteric compounds. III. *tert.*-**Dibenzthienyl amino-alcohols.** A. Burger and H. W. Bryant (*J. Amer. Chem. Soc.*, 1941, **63**, 1054—1057; cf. A., 1939, II, 386).—Dibenzthiophen and phenanthrene are not isosteric. They are not isomorphic; their absorption spectra and pharmacological properties are dissimilar. 3-Bromoacetyldibenzthiophen and the appropriate *sec.* amine in, usually, C_6H_6 give 3-dimethylamino-[*hydrochloride*, m.p. 220—225° (decomp.; vac.)], -diethylamino- [hydrochloride, m.p. 214—215° (decomp.; vac.) (lit. 200—202°)] [with a by-product, m.p. 263—266° (decomp.; vac.)], *-piperidino-*, m.p. 117°, and 3-1′ : 2′ : 3′ : 4′-*tetrahydro*-iso*quinolino-*, m.p. 122—125° [*hydrochloride*, m.p. 244—246° (decomp.; vac.); *hydrobromide*, m.p. 257—259° (decomp.; vac.)], *-acetyldibenzthiophen*, hydrogenated (PtO_2; MeOH) as hydrohalide to 3-β-dimethylamino- [*hydrochloride*, m.p. 228—228·5° (decomp.; vac.); *acetate hydrochloride*, m.p. 206—208° (decomp.; vac.)], *-diethylamino-* (I), m.p. 59—60° [*hydrochloride*, m.p. 163—164°; *acetate hydrochloride*, m.p. 188—192° (decomp.; vac.)], *-piperidino-* (II), m.p. 88—89° [*hydrochloride*, m.p. 225—229° (decomp.; vac.); *acetate hydrochloride*, m.p. 220—225°], and -1′ : 2′ : 3′ : 4′-*tetrahydro*-iso*quinolino-*, m.p. 106—107° [*hydrochloride*, m.p. 243—244° (decomp.; vac.); *hydrobromide*, m.p. 250—252° (decomp.; vac.)], *-α-hydroxyethyldibenzthiophen*. 3-Acetyldibenzthiophen (III), paraformaldehyde, and the appropriate *sec.* amine hydrochloride in boiling *iso*-C_5H_{11}·OH (IV) or *cyclo*hexanol (V) give 3-β-dimethylamino- [*hydrochloride*, m.p. 192—195° (decomp.; vac.)], -diethylamino- [*hydrochloride*, m.p. 150—151°; prep. in (V); in (IV) a non-basic substance, m.p. 82—82·5°, is formed], -piperidino- [*hydrochloride*, m.p. 201—203° (decomp.; vac.)], and -1′ : 2′ : 3′ : 4′-*tetrahydro*iso*quinolino-*, m.p. 106—107° [*hydrochloride*, m.p. 197—198° (decomp.; vac.)], *-propionyldibenzthiophen*, hydrogenated as above to 3-*γ-dimethylamino-* (VI), m.p. 118° (*hydrochloride*, m.p. 137—139°; *acetate hydrochloride*, m.p. 149—150°), *-piperidino-* (VII), m.p. 102° [*hydrochloride*, m.p. 201—201·5° (decomp.; vac.); *acetate hydrochloride*, m.p. 185—186°], and -1′ : 2′ : 3′ : 4′-*tetrahydro*iso*quinolino-*, m.p. 136° [*hydrochloride*, m.p. 183—185°; *acetate hydrochloride*, m.p. 193—196° (decomp.; vac.)], *-β-hydroxy-*n-*propyldibenzthiophen*. 1-*β-Piperidinopropionyl-*, m.p. 112° [*hydrochloride*, m.p. 229—232° (decomp.; vac.)], and 1-*γ-piperidino-β-hydroxy-*n-*propyl-*, m.p. 105°, *-dibenzthiophen* are similarly prepared. Boiling $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ reduces (III) to 3-*α-hydroxyethyldibenzthiophen*, m.p. 76—77° (oily *acetate*). Analgæsic and other physiological properties of (I), (II), (VI), and (VII) are reported. R. S. C.

Preparation and attempted resolution of 2 : 2-dimethylethyleneimine. T. L. Cairns (*J. Amer. Chem. Soc.*, 1941, **63**, 871—872).—NH_2·CMe_2·CH_2·OH (I) distilled with aq. H_2SO_4 (first up to 115°/atm. pressure and later 150—170°/25—30 mm.) gives 2 : 2-*dimethylethyleneimine* (II), b.p. 69—70°, stable to $KMnO_4$ and converted by dil. H_2SO_4 into NH_2·CH_2·CMe_2·OH. *d*-CHMePh·NH_2,HCl and $COCl_2$ in boiling PhMe give *l*-α-phenylethylcarbimide, b.p. 82—83°/12—14 mm., $[\alpha]_D^{24}$ −2° in C_6H_6, which with NH_3–C_6H_6 gives *d*-α-phenylethylcarbamide, m.p. 121—122°, $[\alpha]_D^{25}$ +48·8° in abs. EtOH, and with (II) in C_6H_6 gives d-1-*α-phenylethylcarbamyl*-2 : 2-*dimethylethyleneimine* (III), m.p. 104—105°, $[\alpha]_D^{25}$ +48° in C_6H_6. Mutarotation of (III) occurs in boiling C_6H_6, but is due solely to decomp. R. S. C.

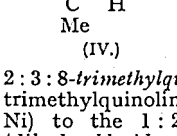
Aminoethanol derivatives possessing local anæsthetic activity. F. C. MacIntosh and T. S. Work (*Quart. J. Pharm.*, 1941, **14**, 16—25).—7 : 1-OMe·$C_{10}H_6$·CO·CH_2·NMe_2 (from the bromide and $NHMe_2$ in MeOH–Et_2O) is reduced (H_2, PtO_2, MeOH–HCl) to 7-methoxy-1-naphthyldimethylaminomethylcarbinol (an oil) [*hydrochloride*, m.p. 209°; *picrate*, m.p. 158° (sinters at 95°)]. Similarly, condensation of COPh·CH_2Br with piperidine (I) and reduction of the resultant base affords *phenylpiperidinomethylcarbinol hydrochloride*, m.p. 195°. C_6H_{13}Ph (prep. from hexoylbenzene by Clemmensen or Wolff–Kishner reduction) with CH_2Cl·COCl and $AlCl_3$ in CS_2 yields p-*hexylphenacyl chloride*, m.p. 32°, b.p. 154—156°/0·9 mm., which with (I) in Et_2O and subsequent reduction affords *p*-hexylphenylpiperidinomethylcarbinol (*picrate*, m.p. 133—135°); similarly PhBu gives p-*butylphenacyl chloride* (II), b.p. 142—144°/2 mm., the corresponding piperidino-ketone (an oil) (III), and *p*-butylphenylpiperidinomethylcarbinol (an oil) (*picrate*, m.p. 137—138°). *p*-Butylphenylethylpiperidinomethylcarbinol (*hydrochloride*, m.p. 178°) was prepared from (III) and MgEtI in Et_2O; the corresponding methylcarbinol (*hydrochloride*, m.p. 186°) was obtained from (II) and MgMeI (which yielded an oil and a cryst. *substance*, $C_{12}H_{16}O$, m.p. 121°) and subsequent treatment of the resulting oil with (I). *α-Chlorotridecan-β-one*, m.p. 46° (from lauryl chloride and CH_2N_2 in Et_2O, the resultant diazoketone, m.p. 44°, being decomposed in Et_2O by dry HCl), with (I) in Et_2O gives a piperidino-ketone, reduced to piperidinomethylundecylcarbinol (*picrate*, m.p. 69—70°). The above compounds of the type OH·CRR′·CH_2·NR″, together with others previously described (A., 1940, II, 356), were examined for local anæsthetic activity (cf. A., 1941, III, 528). F. O. H.

p-**Piperidinobenzonitrile, m.p. 55°.**—See A., 1941, I, 271.

Synthesis of dihydroindole, dihydrothionaphthen, and dihydrobenzofuran. G. M. Bennett and M. M. Hafez (*J.C.S.*, 1941, 287—288).—*o*-Amino-β-phenylethyl alcohol (O-*Bz* derivative, m.p. 168°) when heated with HCl and made alkaline or with $PhSO_2Cl$ and cold aq. alkali gives indoline (*p*-C_6H_4Me·SO_2, m.p. 99°, and *Ac* derivatives, m.p. 105°). Diazotisation of the alcohol in H_2SO_4 and treatment with $NaHCO_3$ affords 2 : 3-dihydrobenzofuran and introduction of S by the Leuckhardt process followed by warming with acid yields dihydrothionaphthen. F. R. S.

Vitamin-B_6.—See B., 1941, III, 161.

Petroleum bases. II. Amino- and hydroxy-derivatives. Chemistry of diazo-oxides. L. R. Modlin, jun., and A. Burger (*J. Amer. Chem. Soc.*, 1941, **63**, 1115—1118).—5-Hydroxy-2 : 3 : 8-trimethylquinoline (I) (A., 1940, II, 288) and HNO_3 (*d* 1·5) at 0° give the 6-NO_2-derivative, m.p. (+EtOH or anhyd.) 152—152·5°, converted by CH_2N_2–EtOH–MeOH into the *Me ether* (II), m.p. 128—129°, also obtained by nitrating 2 : 3 : 8 : 5-$C_{10}H_4Me_3$·OMe at −10°. $SnCl_2$–HCl reduces (II) to 6-*amino-5-methoxy-*, m.p. 137—138° [*hydrochloride*, m.p. 255—259° (decomp.)], converted by HBr into 6-amino-5-hydroxy-2 : 3 : 8-trimethylquinoline (III), unstable [*hydrobromide*, m.p. 330—335° (decomp.; vac.)]. Treating the dihydrobromide of (III) with $NaNO_2$ in 17% HCl at −5° and then with $CO(NH_2)_2$ and pouring the mixture into boiling H_2O gives 2 : 3 : 8-*trimethylquinoline*-6-*diazo*-5-*oxide* (IV), darkens at 167°, decomp. 228° (vac.). With $Na_2S_2O_4$ in boiling aq. EtOH, (IV) gives (I), and with NH_2OH,HCl and C_5H_5N in boiling EtOH gives 2 : 3 : 8-*trimethylquinoline*-5 : 6-*quinonedioxime*, m.p. 189—190° (decomp.; vac.), which in boiling 10% NaOH gives 2 : 3 : 8-*trimethylquinolinofurazan*, m.p. 130°. 5-Amino-2 : 3 : 8-trimethylquinoline is hydrogenated (PtO_2–EtOH or Raney Ni) to the 1 : 2 : 3 : 4-H_4-derivative, b.p. 110°/0·1 mm. (*dihydrochloride*, decomp. >300°; Ac_2, m.p. 152°, and N-*NO*-derivative, cryst.), also obtained from 5-nitro-2 : 3 : 8-trimethylquinoline by H_2–PtO_2–EtOH. Hydrogenation of (I) gives similarly 5-hydroxy-2 : 3 : 8-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoline (65%) [*hydrochloride*, m.p. 258—263° (decomp.)], and an alkali-insol. oil. R. S. C.


(IV.)

Synthesis and pharmacology of dialkylmalonylguanidines. O. H. Miller and L. Fischer (*J. Amer. Pharm. Assoc.*, 1941, **30**, 45—47).—The following were prepared by treatment of the appropriate dialkylmalonic Et_2 ester with guanidine hydrochloride in presence of NaOEt at 80—90° for 60 hr.: *diethyl-*, *ethylisopropyl-*, *ethyl-*n-*butyl-*, *ethylisoamyl-*, and *ethylphenylmalonylguanidine* (all m.p. >300°). For pharmacology of above compounds, cf. A., 1941, III, August. F. O. H.

Pyrimidines. CLXIX. Action of 5 : 5-bromo-oxyhydrouracil on ethylenethiocarbamide. T. B. Johnson and C. O. Edens (*J. Amer. Chem. Soc.*, 1941, **63**, 1058—1060).—5 : 5-Dibromo- or -dichloro-hydroxydihydrouracil in boiling EtOH oxidises ethylenethiocarbamide (I) to $(CH_2$·NH_2,HHal$)_2$, S, and the substance (II), $C_6H_{10}N_4S$, m.p. 218—220°, of Jaffe *et al.* (A., 1894, i, 437). (II) is *di*-4 : 5-*dihydro*-2-*glyoxalinyl sulphide*. It is obtained from (I) (*loc. cit.*) or $(CH_2$·$NH_2)_2$ by

$CSCl_2$, reaction proceeding by way of $\begin{matrix}CH_2\cdot NH\\ CH_2—N\end{matrix}\!\!>\!C\cdot S\cdot CSCl$ and, from (I), $\left[\begin{matrix}CH_2\cdot NH\\ CH_2—N\end{matrix}\!\!>\!C\cdot S\right]_2 CS$. R. S. C.

5-Amino-1-aryl-3-methylpyrazoles. F. Bell (*J.C.S.*, 1941, 285—287).—The methods of preparing 5-amino-1-phenyl-3-methylpyrazole (I) are reviewed; the most satisfactory is from $NHPh\cdot NH_2$ and diacetonitrile, which give cyanoacetonephenylhydrazone, converted by 6N-HCl into (I). Similarly *o*-$C_6H_4Cl\cdot NH\cdot NH_2$ affords *cyanoacetone-o-chlorophenylhydrazone*, m.p. 74—77°, and *5-amino-1-(2′-chlorophenyl)-3-methylpyrazole hydrochloride* ($+2H_2O$), m.p. 123—126°, and 2 : 5-$C_6H_3Cl_2\cdot NH\cdot NH_2$ (II) yields *cyanoacetone-2 : 5-dichlorophenylhydrazone*, m.p. 112—114°, and *5-amino-1-(2′ : 5′-dichlorophenyl)-3-methylpyrazole hydrochloride*, m.p. 214—220°. $CH_2Ac\cdot CO_2Et$ and (II) give *Et acetoacetate 2 : 5-dichlorophenylhydrazone*, m.p. 66—68°, which with $POCl_3$ affords *5-chloro-1-(2′ : 5′-dichlorophenyl)-3-methylpyrazole*, b.p. 195°/25 mm. F. R. S.

Chloral amides. VII. H. W. Hirwe and P. Y. Kulkarni (*Proc. Indian Acad. Sci.*, 1941, **13, A**, 49—52; cf. A., 1940, II, 220).—Chloral and *o*-$NH_2\cdot CO\cdot C_6H_4\cdot NH_2$,HCl at 60—70° yield *4-keto-2-trichloromethyl-1 : 2 : 3 : 4-tetrahydroquinazoline*, m.p. 202° (*Ac* derivative, m.p. 194—195°), stable towards HCl. Chloral, warmed with the appropriate amide, yields *chloral-2-* (I), m.p. 172—173°, *-3-*, m.p. 164—165°, and *-4-acetamido-*, m.p. 259—260°, *-2-*, m.p. 168—169°, *-3-*, m.p. 232—233°, and *-4-benzamido-* (requires long heating), m.p. 212—213°, and *-5-bromo-2-acetamido-* (II), m.p. 171—172°, and *-benzamido-benzamide*, m.p. 171°. (I) with Br in glacial AcOH yields (II), hydrolysed (10% NaOH) to *6-bromo-4-keto-2-methyl-3 : 4-dihydroquinazoline*. A. Li.

Triazine and glyoxaline series. A. H. Cook and D. G. Jones (*J.C.S.*, 1941, 278—282).—Polymerisation of the appropriate nitrile with $ClSO_3H$ affords the kyaphenine; *tri-o-methylkyaphenine*, m.p. 110°, is prepared from *o*-$C_6H_4Me\cdot CN$. *m-Nitrokyaphenine*, m.p. 206°, is obtained by heating a mixture of PhCN, *m*-$NO_2\cdot C_6H_4\cdot COCl$, NH_4Cl, and $AlCl_3$; the *p-compound*, m.p. 218°, is similarly prepared. *m*-$NO_2\cdot C_6H_4\cdot CN$ with BzCl gives *di-m-nitrokyaphenine*, m.p. 253°, and the *p-compound*, m.p. 297°, is obtained similarly, whilst *p*-$NO_2\cdot C_6H_4\cdot CN$ and *p*-$NO_2\cdot C_6H_4\cdot COCl$ yield *dinitrocyanobenzophenone*, m.p. 218°. Nitration (KNO_3–H_2SO_4) of tri-*p*-methylkyaphenine gives the NO_2-derivative, m.p. 239°, whilst with fuming HNO_3 the m-$(NO_2)_3$-compound, m.p. 305—307°, also obtained by polymerisation of 2 : 1 : 4-$NO_2\cdot C_6H_3Me\cdot CN$, is prepared. *Dinitrotri-p-chlorokyaphenine*, m.p. 348°, is formed by nitration. Reduction of the corresponding NO_2-derivative with $NHPh\cdot NH_2$ affords m-, m.p. 214°, and p-*amino-*, m.p. 273° (decomp.) (*Ac* derivative, m.p. 315°), and m-*aminotri-*p-*methyl-*, m.p. 231°, and *di-*m-*nitrotri-*m-*amino-*p-*methyl-kyaphenine*, m.p. 261°. Reduction (Zn–AcOH) of tri-*p*-chlorokyaphenine yields *tri-*p-*chlorolophine*, m.p. 268°. Condensation of benzil with the appropriate aldehyde and NH_4OAc gives 4 : 5-*diphenyl-2-ethyl-*, m.p. 229°, 4 : 5-*diphenyl-*2-iso*propyl-*, m.p. 248°, 2-o-*hydroxyphenyl-*4 : 5-*diphenyl-*, m.p. 209°, 2-p-*methoxyphenyl-*4 : 5-*diphenyl-*, m.p. 229°, 2-o-, m.p. 230°, 2-m-, m.p. 309°, and 2-p-*nitrophenyl-*4 : 5-*diphenyl-*, m.p. 240°, 4-p-*nitrophenyl-*2 : 5-*diphenyl-*, m.p. 229°, 2-o-*hydroxyphenyl-*4-p-*nitrophenyl-*5-*phenyl-*, m.p. 217°, and 2-m-*nitrophenyl-*4-p-*nitrophenyl-*5-*phenyl-glyoxaline*, m.p. 226° and 256°, and *2-phenyl-*, m.p. 314°, and 2-o-*nitrophenyl-*4 : 5 : 9′ : 10′-*phenanthriminazole*, m.p. 267°. Reduction ($NHPh\cdot NH_2$) affords 2-o-, m.p. 196°, and 2-m-*aminophenyl-*4 : 5-*diphenyl-*, m.p. 283° (decomp.), and 4-p-*aminophenyl-*2 : 5-*diphenyl-glyoxaline*, m.p. 245° (decomp.). Most of the new glyoxalines exhibit chemiluminescent properties recalling those of lophine. F. R. S.

Bile pigments from choleglobin and verdohæmochromogen. —See A., 1941, III, 447.

Addition compounds of morpholine. H. M. Haendler and G. McP. Smith (*J. Amer. Chem. Soc.*, 1941, **63**, 1164).—Morpholine gives 2 : 1 additive *compounds* with $ZnCl_2$, softens at 200—210°, later melts, $ZnBr_2$, decomp. 230—240°, $CdBr_2$, decomp. 250—252°, CdI_2, decomp. 205—210°, $HgBr_2$, decomp. 131—135°, $CdCl_2$, and $HgCl_2$. Co and Cu^{II} halides react, but the Cu^{II} compounds are very sensitive to H_2O. R. S. C.

Reactions of monoalkylanilines with ββ-dichlorodiethyl ether. 4-Phenylmorpholine. H. C. Brill, C. N. Webb, and H. S. Hakbedel (*J. Amer. Chem. Soc.*, 1941, **63**, 971—972).—$(Cl\cdot[CH_2]_2)_2O$ and NHPhAlk give *N*-phenylmorpholine (I), the yield being higher if Alk is Me or Et than if it is Bu^{α} or *iso*amyl. The alkiodide of (I) may be an intermediate. R. S. C.

Stable derivative of 4-amino-3-hydroxybenzenesulphonamides. J. V. Scudi and R. P. Buhs (*J. Amer. Chem. Soc.*, 1941, **63**, 879—880).—Benzoxazolone (prep. in 50% yield from *o*-$OH\cdot C_6H_4\cdot NH_2$ by $COCl_2$–C_5H_5N) and $ClSO_3H$ at 10—15° and later 60° give the 5-sulphonyl chloride, m.p. 182—183° (corr.), from which aq. NH_3 and boiling NH_2Ph–dioxan give benzoxazolone-5-sulphon-amide (I), m.p. 269—270° (decomp.), and *-anilide*, m.p. 215—216° (corr.), respectively. Ingestion of (I) does not protect mice against hæmolytic streptococci; examination of the urine shows that the oxazolone ring is not cleaved. R. S. C.

Dimorpholine salts.—See B., 1941, II, 178.

Thiazoline-*m*-cresol. Functional derivatives and substitution products. W. F. Hart and J. B. Niederl (*J. Amer. Chem. Soc.*, 1941, **63**, 945—947).—2-5′-Hydroxy-*o*-tolyl-5-methylthiazoline (A., 1939, II, 347) gives by standard methods the *methiodide*, m.p. 166°, *Me*, m.p. 107—108° (*picrate*, m.p. 117°; *methiodide*, m.p. 160°), Et (*hydrochloride*, m.p. 156°; *picrate*, m.p. 118°; *methiodide*, m.p. 148°), Pr^{α} (*hydrochloride*, m.p. 183°; *picrate*, m.p. 121°; *methiodide*, m.p. 101°), Pr^{β} (*hydrochloride*, m.p. 190°; *picrate*, m.p. 107°; *methiodide*, m.p. 93°), Bu^{α} (*hydrochloride*, m.p. 180°; *picrate*, m.p. 111°; *methiodide*, m.p. 108°), allyl (*hydrochloride*, m.p. 163°; *picrate*, m.p. 112°; *methiodide*, m.p. 117°), n-$C_{12}H_{25}$ (*hydrochloride*, m.p. 148°; *methiodide*, m.p. 82°), cetyl (*hydrochloride*, m.p. 143°; *methiodide*, m.p. 66°), and $NEt_2\cdot[CH_2]_2$ (*dihydrochloride*, m.p. 189°) ether, oxyacetic acid derivative [carboxymethyl ether?] (*hydrochloride*, m.p. 230°; *Na* salt; *Et* ester *hydrochloride*, m.p. 184°), *phenylurethane*, m.p. 105° (*hydrochloride*, m.p. 167°), *NO*$_2$-, m.p. 144° (*hydrochloride*, m.p. 180°), and *NH*$_2$-derivative, m.p. 224° (*dihydrochloride*, m.p. 250°). 15% oleum at 100° gives the *sulphonic acid*, m.p. 300° (*Na* salt). NaOMe–MeOH at 80° and then, after removal of the MeOH, CO_2 at 170—175° gives the *4′-carboxylic acid*, m.p. 219—220° [*hydrochloride*, m.p. 225—230°; *Na* salt; *Me*, m.p. 76—77° (*hydrochloride*, m.p. 181—183°; *methiodide*, m.p. 172—175°), and *Et* ester, m.p. 77—78° (*hydrochloride*, m.p. 173—175°; *methiodide*, m.p. 161—163°; *picrate*, m.p. 142—143°)]. R. S. C.

Amino-analogue of vitamin-B_1. D. Price and F. D. Pickel (*J. Amer. Chem. Soc.*, 1941, **63**, 1067—1069).—4-Methyl-5-thiazolylacetamide (prep. from the Et ester by aq. NH_3 at room temp.) and $POCl_3$ at 115—120° give *4-methyl-5-thiazolylacetonitrile* (I), b.p. 92—93°/2 mm. (*picrate*, m.p. 171°), hydrogenated (Raney Ni–EtOH or Pd– or ZrO_2–AcOH–HCl) to 4-methyl-5-β-aminoethylthiazole, b.p. 82—85°/2 mm. (*picrate*, m.p. 227°), which with 6-amino-2-methyl-5-bromomethylpyrimidine dihydrobromide in $Bu^{\alpha}OH$ at 120—125° gives *3-6′-amino-2′-methyl-5′-pyrimidylmethyl-4-methyl-5-β-aminoethylthiazolium bromide dihydrobromide* (II), m.p. 250—251° (derived picrate, m.p. 204—206°). (I) and the appropriate thiazole derivative give similarly *3-6′-amino-2′-methylpyrimidylmethyl-4-methyl-5-cyanomethylthiazolium bromide hydrobromide* (III), $+H_2O$, m.p. 231—232° (derived picrate, m.p. 199—200°). (II) and, by hydrolysis, (III) give the Pauly reaction. (II), but not (III), gives the thiochrome reaction. (II) has no vitamin-B_1 activity. R. S. C.

***Erythrophleum* alkaloids. IV. Coumingine, a crystalline alkaloid from the bark of *E. couminga* (H. Baillon) and its relationship to cassaine.** L. Ruzicka, G. Dalma, and W. E. Scott (*Helv. Chim. Acta*, 1941, **24**, 63—76).—The powdered bark is extracted with Et_2O and the alkaloid mixture is crystallised from $COMe_2$–H_2O; the crude alkaloid is purified by adsorption on Al_2O_3 followed by elution with C_6H_6–Et_2O and crystallisation from Et_2O, thereby giving homogeneous *coumingine* (I), $C_{28}H_{45}O_6N$, m.p. 142°, $[\alpha]_D^{20}$ −70°±1° in 95% EtOH [*hydrochloride*, m.p. 195° (vac.); *oxime*, m.p. 165°]. Pure (I) does not react with cold or hot Ac_2O–C_5H_5N whereas crude (I) gives an *acetate*, $C_{30}H_{47}O_7N$, m.p. 154—155°. Hydrogenation (PtO_2 in AcOH at room temp.) of (I) affords *dihydrocoumingine*, m.p. 95—96°, $[\alpha]_D^{20}$ +8°±1° in EtOH (very hygroscopic *hydrochloride*, m.p. 160—162°). Acid hydrolysis of (I) gives *coumingic acid* (II), $C_{24}H_{36}O_6$, m.p. 200° (vac.),

$[\alpha]_D^{20}$ $-81°\pm3°$ in 95% EtOH [*Me* ester, m.p. 217—218° (high vac.), $[\alpha]_D^{20}$ $-83°\pm1°$ in 95% EtOH, and its *oxime*, m.p. 124—125°], and $NMe_2\cdot[CH_2]_2\cdot OH$. Alkaline hydrolysis of (I) affords cassaic acid (III), m.p. 223—224° (high vac.), $[\alpha]_D^{20}$ $-123°\pm1°$ in 95% EtOH, also identified as the Me ester, m.p. 188—189°, $[\alpha]_D^{20}$ $-124°\pm2°$ in 95% EtOH, and its Ac derivative, new m.p. 150°; (III) is also obtained by the alkaline hydrolysis of (II). (III) is oxidised by CrO_3 in AcOH to diketocassenic acid, m.p. 249° (high vac.), $[\alpha]_D^{20}$ $-152°\pm2°$ in 95% EtOH (Me ester, m.p. 132—133°, $[\alpha]_D^{20}$ $-156°\pm2°$ in 95% EtOH). (I) is an ester of cassaine with an acid $C_4H_8O_3$ which contains the O atom of unknown function in (I).

H. W.

VI.—ORGANO-METALLIC COMPOUNDS.

Preparation of organo-bismuth compounds from diazonium compounds. H. Gilman and H. L. Yablunky (*J. Amer. Chem. Soc.*, 1941, **63**, 949—954).—Determination of Bi in org. compounds is modified. *Compounds*, (*a*) *o*-$C_6H_4Me\cdot N_2Cl,BiCl_3$, decomp. 82°, (*b*) $(ArN_2Cl)_2,BiCl_3$ in which Ar = Ph, decomp. 94°, α-, decomp. 120°, and β-$C_{10}H_7$, decomp. 118°, *o*-, decomp. 160°, and *p*-C_6H_4Cl, decomp. 154°, *o*-, decomp. 155°, and *p*-C_6H_4Br, decomp. 147° (fuses at 120°), *p*-C_6H_4I, decomp. 129°, *o*-, decomp. 153°, and *p*-$C_6H_4\cdot OMe$, decomp. 145°, *o*-$C_6H_4\cdot CO_2Me$ (I), decomp. 122°, *o*- (II), decomp. 115°, and *p*-$C_6H_4\cdot CO_2Et$, unstable, decomp. 91°, and *p*-$C_6H_4\cdot SO_2\cdot NH_2$, decomp. 123°, and (*c*) $(ArN_2Cl)_3,BiCl_3$ in which Ar = *p*-tolyl, decomp. 127° (fuses at 110°), and *p*-C_6H_4Ph, decomp. 121°, are prepared. With (best) Cu-bronze in abs. EtOH and later N_2H_4, these compounds usually give $BiAr_3$ in poor yield, examples being Ar = p-C_6H_4Br (III), m.p. 144·5—145°, Ph, *o*- and *p*-tolyl (IV), α-$C_{10}H_7$, *p*-C_6H_4Cl, *o*- and *p*-$C_6H_4\cdot OMe$; some ArCl and $(ArN:)_2$ are also formed. With Cu-bronze in abs. EtOH, (I) gives *Bi di-o-carbomethoxyphenyl chloride* (10·3%), m.p. 180—181°, and *o-carbomethoxyphenyl dichloride* (1·95%), m.p. 220—221°, but (II) gives *Bi di-o-carbethoxyphenyl chloride* (6·5%), m.p. 147—148°; these chlorides are unusually stable. Presence of NaI during the decomp. leads to $BiPh_3$, but not (III) or (IV). Similar decomp. of *p*-$C_6H_4Br\cdot N_2Cl,ZnCl_2$ gives *p*-C_6H_4BrCl (46·7%) and of PhN_2Cl,BF_3 gives (NPh_2).

R. S. C.

Organic mercury derivatives of basic triphenylmethane dyes: dimercuri-derivatives of malachite-green. L. Chalkley (*J. Amer. Chem. Soc.*, 1941, **63**, 981—987).—Colourless, but not coloured, compounds of the $CHPh_3$ dye series are readily mercurated. The coloured compounds resemble quaternary salts in their resistance to $Hg(OAc)_2$. (*p*-$NMe_2\cdot C_6H_4)_2CPh\cdot CN$ (I) and $Hg(OAc)_2$–AcOH in boiling EtOAc, followed by KOH–MeOH, give 4 : 4′-*bisdimethylamino*-3-*hydroxymercuri*-3′-*methoxymercuritriphenylacetonitrile*, decomp. >200° (variable), converted by irradiation (ultra-violet) in 1% AcOH–MeOH into the impure dye, 4 : 4′-bisdimethylamino-3-hydroxymercuri-3′-cyanomercuritriphenylcarbinol (cf. A., 1940, II, 239). A more convenient synthesis utilises acid-labile colourless compounds CAr_3X (X = OH, OMe, NH_2), which in "non-ionising" org. solvents exist mainly in the colourless form, are thus readily mercurated, and are then transformed into the coloured mercurials by acid in, *e.g.*, H_2O or EtOH. Isolation of the coloured mercurial is often difficult, *e.g.*, [4 : 3-$NMe_2\cdot C_6H_3(Hg\cdot OAc)]_2CPh\cdot CN$ is more sol. in EtOH or EtOAc than is (I). Details are given for conversion of (*p*-$NMe_2\cdot C_6H_4)_2CPh\cdot OH$ by $Hg(OAc)_2$ in EtOAc at 70° and later 56° into 4 : 4′-*bisdimethylamino*-3 : 3′-*di(acetoxymercuri)triphenylcarbinol*, +*x*AcOH and solvent-free, decomp. >~115°, hydrolysed by 2N-KOH–MeOH to the (*HgOH*)$_2$-compound (II), decomp. >200°, whence NaCl–MeOH–H_2O–AcOH (little) ppts. the impure $(HgCl)_2$-compound. Hg_1 derivatives cannot be obtained free from Hg_2 compounds. In solutions of the Hg compounds the coloured and colourless forms are in equilibrium, the relative amounts depending on the concn. of acid present and on the temp. (more dye at higher temp.); this complicates isolation. Aq. solutions of (I) become coloured at p_H 13—11·4, but those of (II) only at p_H 7. In acid baths, (II) dyes silk at 1 in 5×10^6, but the colour is somewhat lighter than is given by (I). In weakly alkaline or neutral baths, (II) exhausts onto silk, giving only slightly coloured fibres. The Hg derivatives are surface-active.

R. S. C.

VII.—PROTEINS.

Origin of the humin formed by the acid hydrolysis of proteins. IX. Hydrolysis in presence of djenkolic and thiazolidine-4-carboxylic acids. H. A. Lillevik and W. M. Sandstrom (*J. Amer. Chem. Soc.*, 1941, **63**, 1028—1030; cf. A., 1924, i, 762).—Hydrolysis of djenkolic (I) or thiazolidine-4-carboxylic acid by 20% HCl gives CH_2O and cysteine + cystine (isolated), the reaction being confirmed by polarographic and colorimetric analysis and by condensation of CH_2O with tryptophan (II). (I) may be the aldehyde responsible for humin formation from gelatin and (II). $(CH_2O)_3$ is less effective than these acids.

R. S. C.

Separation of amino-acids by means of copper salts. III. Hydrolysis of gliadin. Dicarboxylate fraction; isolation of *r*-glutamic acid as hydrolysis product. B. W. Town (*Biochem. J.*, 1941, **35**, 417—432).—40·4% of glutamic acid has been isolated from gliadin; 5% of this is obtained as *r*- and 95% as *l*(+)-glutamic acid. *r*-Glutamic acid gives a 3 : 5-*dinitrobenzoyl* derivative, m.p. 204° as compared with 104° for the same derivative of the *dl*-mixture, which, on hydrolysis and rebenzoylation, gives only 4·5% of the compound of m.p. 204°. Similar treatment of the high-melting derivative yields 42·6% of the same compound, thus indicating the presence of the *r*-compound as a definite hydrolysis product. 0·43% of aspartic acid and 0·18% of serine have also been isolated from the dicarboxylic acid fraction, the presence of the latter tending to interfere with crystallisation of the other acids.

P. G. M.

Hydrogen linking in protein structure.—See A., 1941, I, 245.

VIII.—ANALYSIS.

Electric heating mortar for use in carbon and hydrogen micro-combustions.—See A., 1941, I, 283.

Application of the grating microspectrograph to the problem of identifying organic compounds.—See A., 1941, I, 282.

Colour reactions of aliphatic acids. G. Roeder (*J. Amer. Pharm. Assoc.*, 1941, **30**, 74—76).—Colour reactions of the following substances with hot Ac_2O in presence of an org. base or an alkali salt of a carboxylic acid are described: malonic, aconitic, citric, cetylcitric, tartaric, acetonedicarboxylic, ascorbic, and *d-iso*ascorbic acid, glucono-*d*- and glucoheptono-lactone. Hydroxydimethylbutyrolactone does not give a colour.

F. O. H.

Determination of threonine by periodate. L. A. Shinn and B. H. Nicolet (*J. Biol. Chem.*, 1941, **138**, 91—96).—Threonine (I) is determined in protein hydrolysates by oxidation (HIO_4), removal of MeCHO in a current of CO_2, absorption in $NaHSO_3$, and titration. Casein contains 3·5% and gelatin 1·4% of (I).

A. Li.

Decolorisation of acid digestion mixtures for determination of nicotinic acid. T. E. Friedemann and C. J. Barborka (*J. Biol. Chem.*, 1941, **138**, 785—786).—A decolorisation technique is described involving digestion with dil. HCl and treatment with $ZnSO_4$ and NaOH.

A. Li.

Determination of carotene.—See A., 1941, III, 455.

Simplification of the Petering–Wolman–Hibbard method for determination of chlorophyll and carotene. H. G. Petering, E. J. Benne, and P. W. Morgal (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 236; cf. A., 1940, III, 549).—Instead of adding $Ba(OH)_2,8H_2O$ to the aq.-$COMe_2$ extract, saturated aq. $Ba(OH)_2$ is added to the $COMe_2$ extract in amount sufficient to remove all the chlorophyll, and the mixture treated as in the original procedure (*loc. cit.*).

J. D. R.

Detection of quinicine and cinchonicine. J. W. Millar and S. J. Dean (*J. Amer. Pharm. Assoc.*, 1941, **30**, 52—53).—$PhN_2\cdot SO_3H$ reagent gives reliable tests for quinicine (I) and cinchonicine (II) in aq. or EtOH solution and in presence of the parent alkaloid or alkaloidal salts; dinitrothiophen reagent is also satisfactory, excepting in presence of the alkaloidal salts. A modified Lipkin test (Br–aq. NH_3, followed by extraction with $CHCl_3$) differentiates between quinine and (I) and cinchonine and (II), whilst $K_4Fe(CN)_6$ reagent differentiates between (I) and (II).

F. O. H.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

AUGUST, 1941.

I.—ALIPHATIC.

Temperature coefficient of density and refractive index for hydrocarbons in the liquid state.—See A., 1941, I, 295.

Isomerisation of normal butane by the action of aluminium chloride. O. Ferrari (*Rev. Fac. Cienc. Quím., La Plata*, 1940, **15**, 297—305).—The optimum conditions for the conversion of *n*- into *iso*-C_4H_{10} require contact for 30 min. at 120° with $AlCl_3$ containing 3·75% of H_2O. The yield is 50% and the method can be applied industrially as a continuous process. The reaction velocity is decreased by addition of anhyd. or conc. HCl. F. R. G.

Preparation of tetramethylene bromide. S. Fried and R. D. Kleene (*J. Amer. Chem. Soc.*, 1940, **62**, 3258).—$Br{\cdot}[CH_2]_4{\cdot}Br$ is best prepared by decarboxylating 2-furoic acid by CuO–quinoline, hydrogenating (Pd–PdO) furan to tetrahydrofuran (95%), and heating this at 150° with the theoretical amount of dry HBr (70% yield). R. S. C.

Polarographic study of aliphatic nitro-compounds. T. de Vries and R. W. Ivett (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 339—340).—The reductions of $MeNO_2$, $EtNO_2$, $Pr^{\alpha}NO_2$, $Bu^{\alpha}NO_2$, $Pr^{\beta}NO_2$, and $Bu^{\beta}NO_2$ at a dropping Hg cathode using a manually operated polarograph in the concn. range of 0·0005—0·017M. are described. The galvanometer deflexions are ∝ concn. of NO_2-compound within a few %. In neutral 0·05N-Na_2SO_4 partial conversion into *aci*-NO_2-compound causes deviation from a linear relationship. The half-wave potentials are also given, but it is not possible to determine the compounds separately in the presence of each other. J. D. R.

Synthesis of monohydric unsaturated alcohols containing two or three double linkings. P. S. Pelkis and Z. N. Pazenko (*Ber. Inst. Chem. Akad. Wiss. Ukrain.*, 1940, **6**, 311—342).—$\Delta^{\alpha\epsilon}$-*Heptadien*-δ-*ol*, b.p. 68—68·2°/24 mm., was prepared by adding allyl bromide and crotonaldehyde to Mg under Et_2O. From $CO(CH{:}CHPh)_2$ and allyl bromide in the presence of Mg a *ketone*, $C_{37}H_{34}O_2$ (I), m.p. 89° [*p-bromophenylhydrazone*, $C_{49}H_{44}N_4Br_2$, m.p. 180—185° (decomp.); two *bromides*, $C_{37}H_{34}O_2Br_2$ and $C_{37}H_{34}O_2Br_6$], was obtained. When fresh, (I) contains enol groups which disappear within a few days. J. J. B.

α-Bromo-*sec.*-alkyl ketones. II. Reaction of γ-bromo-γ-methylbutan-β-one with magnesium methyl iodide. R B. Greenburg and J. G. Aston (*J. Amer. Chem. Soc.*, 1940, **62**, 3135; cf. A., 1941, II, 4).—Addition of MgMeI to $COMe{\cdot}CMe_2Br$ is unhindered, giving 62% of $CMe_2Bu^{\gamma}{\cdot}OH$. R. S. C.

Oxidation of polyhydric alcohols by biological and non-biological means. J. E. Hunter, jun. (*Iowa State Coll. J. Sci.*, 1940, **15**, 78—81).—Primary and *sec.* alcohols in solution were oxidised electrochemically, using metal or C electrodes and a low c.d. $\cdot CH_2{\cdot}OH$ and $>CH{\cdot}OH$ are oxidised equally in a Pb–RSO_4 cell, whereas in a C–RCl cell $>CH{\cdot}OH$ is readily oxidised and $\cdot CH_2{\cdot}OH$ scarcely reacts. Polyhydric alcohols oxidised in presence of C electrodes formed ketoses but no aldehyde, and vice versa with Pb electrodes. Oxidations catalysed by V_2O_5 produced pentoses. J. L. D.

Solid derivatives of monoalkyl ethers of ethylene glycol and diethylene glycol. II. J. F. Manning and J. P. Mason (*J. Amer. Chem. Soc.*, 1940, **62**, 3136—3139; cf. A., 1940, II, 296).—$OH{\cdot}[CH_2]_2{\cdot}OR$ and $OH{\cdot}[CH_2]_2{\cdot}O{\cdot}[CH_2]_2{\cdot}OR$ are best identified as *p*-nitrophenylurethanes. The following are reported. *β-Methoxyethyl α-naphthylurethane*, m.p. 112·5—113·5°, *diphenylurethane*, m.p. 50·3—50·8°, p-*nitrophenylurethane*, m.p. 111—111·4°, *anthranilate*, b.p. 168—172°/7 mm. (*picryl*, m.p. 126°, and *Bz* derivative, m.p. 107—107·2°), and *4-nitro-2-aminophenyl ether*, m.p. 94—95°. *β-Ethoxyethyl α-naphthylurethane*, m.p. 67·3—67·5°, *diphenylurethane* (prep. with difficulty), m.p. 50·8—51°, p-*nitrophenylurethane*, m.p. 79·4—80·1°, *anthranilate*, b.p. 173—175°/8 mm. (*picryl*, m.p. 122·5—123°, and *Bz* derivative, m.p. 61·5—62°), and *4-nitro-2-aminophenyl ether*, m.p. 104°. *β-Butoxy-*, m.p. 58·7—59·1°, *β-β'-methoxyethoxy-*, m.p. 73·4—73·7°, *β-β'-ethoxyethoxy-*, m.p. 65·8—66·3°, and *β-β'-butoxyethoxy-*, m.p. 54·5—55·3°, *-ethyl* p-*nitrophenylurethane*. *β-Butoxy-*, b.p. 194—195°/10 mm. (*picryl* derivative, m.p. 96·5—97°), *β-β'-methoxyethoxy-*, b.p. 208—210°/10 mm. (*picryl* derivative, m.p. 82·5—83°), *β-β'-ethoxyethoxy-*, b.p. 210—214°/9 mm. (*picryl* derivative, m.p. 96·8°), and *β-β'-butoxyethoxy-*, b.p. 222—225°/10 mm. (*picryl* derivative, m.p. 45·5—46°), *-ethyl anthranilate*. *4-Nitro-2-aminophenyl β-butoxy-*, m.p. 66°, *β-β'-methoxyethoxy-*, m.p. 70—71°, and *β-β'-ethoxyethoxy-*, m.p. 84—85°, *-ethyl ether*. R. S. C.

Glyceryl maleates. I. A. J. Drinberg and V. V. Shebrovski (*J. Appl. Chem. Russ.*, 1940, **13**, 1442—1448).—Glycerol and maleic anhydride condense at 200—270° to esters $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}[CO_2{\cdot}CH{:}CH{\cdot}CO_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O]_nH$, where *n* is 1—7. The esters are opalescent or milky gels. R. T.

Action of phosgene on thiodiglycol. P. Y. Chao (*J. Chinese Chem. Soc.*, 1940, 7, 102—104).—$S([CH_2]_2{\cdot}OH)_2$ with $COCl_2$ in $CHCl_3$ gives pure $S([CH_2]_2{\cdot}Cl)_2$ with a trace of $S[(CH_2)_2]_2S$. A. Li.

Radioactive organic bromine compounds. S. D. Chatterjee and D. K. Banerjee (*J. Indian Chem. Soc.*, 1940, **17**, 712—714).—By irradiating $C_2H_4Br_2$ with slow neutrons from Ra and Be, and then adding Br and oleic acid, PhOMe, or NHAcPh, dibromo-oleic acid containing a high concn. of radioactive Br, and $C_6H_4Br{\cdot}OMe$ and p-$C_6H_4Br{\cdot}NHAc$ with lower activity, have been prepared. PBr_3 is activated rapidly by exchange of Br atoms with EtBr previously irradiated with slow neutrons. J. W. S.

Calculation of m.p. of fatty acids. C. L. Tseng, C. E. Sun, and S. T. Li (*J. Chinese Chem. Soc.*, 1940, **7**, 62—64; cf. A., 1937, I, 505).—The equations (*a*) $75{\cdot}2 - \theta_m = 109{\cdot}7(2e^{-(n-5)\alpha} - e^{-2(n-5)\alpha})$ and (*b*) $75{\cdot}2 - \theta_m = 109{\cdot}7(2e^{-(n-4)\alpha} - 2e^{-2(n-4)\alpha})$, in which *n* denotes the no. of C atoms and $\alpha = 0{\cdot}23$, are used to calculate the m.p., θ_m, of the first 19 fatty acids, (*a*) being for odd and (*b*) for even *n*. There is fairly good agreement with experimental vals. for $n > 4$. F. L. U.

Adsorption analysis. II. Adsorption of higher fatty acids. III. Relation between adsorption isotherm and position on the adsorption column. H G. Cassidy (*J. Amer. Chem. Soc.*, 1940, **62**, 3073—3076, 3076—3079; cf. A., 1939, I, 341).—II. Lauric, myristic, palmitic, and stearic acids differ in relative ease of adsorption, *e.g.*, on Al_2O_3, MgO, " active clay," SiO_2 gel, and C. Different varieties of adsorbent behave differently; *e.g.*, varieties of C are found which (*a*) adsorb the acids equally, or adsorb more strongly the acids of (*b*) lower or (*c*) higher mol. wt.

III. Positions taken by the above-named acids on chromatograms prepared from mixtures do not always agree with expectations from the adsorption isotherms. R. S. C.

M.p. of binary mixtures of oleic, linoleic, and linolenic acids.—See A., 1941, I, 300.

$\Delta^{\alpha\epsilon}$-Phytadienoic acid and enzymic dehydrogenation of phytanic, phytenic, and phytadienoic acid. P. Karrer and H. Koenig (*Helv. Chim. Acta*, 1941, **24**, 304—309).—ζ_{K0}-Trimethyl-Δ^{ϵ}-pentadecen-β-one is converted by $CH_2Br{\cdot}CO_2Et$

and Zn–Cu in PhMe into *Et β-hydroxy-βζκο-tetramethyl-Δ$^{\epsilon}$-hexadecenoate*, b.p. 169—170°/0·07 mm. This is transformed by PBr_3 in abs. light petroleum into the corresponding Br-ester, which is converted by alkali into *β$^{\alpha\epsilon}$*-phytadienoic acid, (I), b.p. 164°/0·25 mm. Phytanic acid, phytenic acid, and (I) show reducing action when the liver or muscle enzyme solution is activated according to Lang. H. W.

Electrochemical experiments with maleic acid. F. Fichter and A. Petrovitch (*Helv. Chim. Acta*, 1941, **24**, 549—551).—Org. nitrates are not obtained by the electrolysis of aq. solutions of K maleate and KNO_3 or of solutions of maleic acid (I) and $Ca(NO_3)_2$ in $COMe_2$. The concn. of (I) is varied between 1·27N. and 4N. and that of nitrate between 0·9N. and 1·5N. The ratio of the yield of C_2H_2 by the electrolysis of maleate in MeOH–C_5H_5N and H_2O is ~3 : 2. Electrolysis cannot be effected in MeOH alone, since the anode becomes rapidly covered with an insol. deposit; this can be remedied by addition of C_5H_5N, which, however, diminishes the yield of C_2H_2 when present in excessive amount. H. W.

Δ$^{\alpha}$-Nonene-α*ι*-dicarboxylic acid. F. Bergman (*J. Amer. Chem. Soc.*, 1940, **62**, 3255).—Crude $CO_2H·[CH_2]_7·CHO$ (I) [from θ*ι*-dihydroxystearic acid and $Pb(OAc)_4$ in C_6H_6], $CH_2(CO_2H)_2$, C_5H_5N, and a little piperidine (II) at the b.p. give CO_2 and *Δ$^{\alpha}$-nonene-α*ι*-dicarboxylic acid* (24%), m.p. 94° (*dichloride*, b.p. 184°/2 mm., with "septamide" gives the *substance*, $C_{23}H_{30}O_6N_4S_2$, m.p. 225°; *diamide*, m.p. 160—161°). (I), $CN·CH_2·CO_2H$ (III), C_5H_5N, and a little (II) give similarly *α-cyano-Δ$^{\alpha}$-nonene-ι-carboxylic acid*, b.p. 185—190°/1 mm. $Me·[CH_2]_7·CHO$ and (III) give similarly *Δ$^{\alpha}$-undecononitrile*, b.p. 105°/4 mm. R. S. C.

Synthesis of methyl vinyl ketone by hydration of vinylacetylene. A. N. Tschurbakov and V. N. Riazantzev (*J. Appl. Chem. Russ.*, 1940, **13**, 1464—1469).—$COMe·CH:CH_2$ (I) is obtained in 93% yield by gradual addition of $CH:C·CH:CH_2$ to a solution of $HgSO_4$ and $Fe_2(SO_4)_3$ in 7% H_2SO_4 at 60—80°. $OH·[CH_2]_2·COMe$, obtained as a by-product, is converted into (I) by dehydration. Hg is deposited as a sludge during the reaction. R. T.

Molecular compound of dihydroxyacetone and sodium chloride. L. M. Utkin (*Biochimia*, 1939, **4**, 600—606).—A 1 : 2 *compound* of NaCl and $CO(CH_2·OH)_2$ (I), m.p. 104—105° (decomp.), is obtained from saturated aq. NaCl containing excess of (I). R. T.

Catalysed cleavage of diacetone alcohol and other ketols and unsaturated ketones. S. H. McAllister, W. A. Bailey, jun., and C. M. Bouton (*J. Amer. Chem. Soc.*, 1940, **62**, 3210—3215).—Passage of $OH·CMe_2·CH_2·COMe$ (I) over P_2O_5–H_3PO_4–SiO_2 at 265° gives $CMe_2:CH_2$ + AcOH with small amounts of $CMe_2:CH·COMe$ (II), $COMe_2$, di- and poly-*iso*butylene. Low temp. and rapid feed rate lower the yields owing to unaltered (I). High temp. and slow feed rate lower the yield owing to reversion of (I) to $COMe_2$. (II) very slowly yields $CMe_2:CH_2$ and keten, but simultaneous passage of H_2O causes rapid formation of $CMe_2:CH_2$ and AcOH, this reaction being hydrolytic and faster than that of (I). It follows that decomp. of (I) proceeds by dehydration to (II) and subsequent hydrolytic fission thereof. Temp. along the catalyst bed shows dehydration of (I) to be endothermic and hydrolytic fission of (II) exothermic. $OH·CHMe·CH_2·COMe$ (III) (prep. from $COMe_2$ and MeCHO by CaO at 10°) gives 45% of AcOH + C_3H_8, 5% of $COMe_2$ + MeCHO, and 50% of $CHMe:CH·COMe$. $OH·CHMe·COMe$ gives a trace of acid and mainly $CH_2:CH·COMe$ which resinifies on the catalyst. The C_8-ketol (IV) (prep. from COMeEt by soda–lime at 10°), b.p. 77—78°/5—6 mm., gives $CH_2:CMeEt$, $CHMe:CMeEt$, $EtCO_2H$, and AcOH, 7% of COMeEt, and ~68% of unsaturated ketones. The unsaturated ketones obtained from (IV) by $KHSO_4$ give the same fission products. (IV) is thus a mixture of $OH·CMeEt·CH_2·COEt$ and $OH·CMeEt·CHMe·COMe$. The unsaturated C_8-ketone, b.p. 165—169°, obtained as by-product in the prep. of (III), gives C_5H_8, b.p. 30—36°, and $EtCO_2H$. The reaction may be used to deduce structure unless rearrangement is suspected. R. S. C.

***d*-Glucose *O*-methyl *S*-ethyl monothioacetal.** M. L. Wolfrom, D. I. Weisblat, and A. R. Hanze (*J. Amer. Chem. Soc.*, 1940, **62**, 3246—3250).—*d*-Galactose Et_2 mercaptal penta-acetate and boiling AcBr give 1-*bromo*-1-*ethylthiol*-aldehydo-d-*galactose penta-acetate* (I), m.p. 101°, $[\alpha]_D^{22}$ −13·4° (in this and other cases $[\alpha]_D$ in EtOH-free $CHCl_3$), and 1-*ethylthiol*-aldehydo-d-*galactose hexa-acetate* (II), m.p. 94—95·5°, $[\alpha]_D^{22}$ +38·4°. Pure (I) is stable in vac., reduces Fehling's solution, in boiling dil. acid or alkali evolves EtSH, and with Ag_2CO_3 in abs. EtOH gives galactose Et_2 monothioacetal penta-acetate. *aldehydo-d*-Galactose penta-acetate in boiling EtSH gives aldehydo-d-*galactose Et monothiohemiacetal penta-acetate*, m.p. 137—139°, $[\alpha]_D^{24}$ −1·5° (reduces Fehling's solution; in boiling EtOH slowly exchanges SEt for OEt), which with Ac_2O–C_5H_5N at 0° gives (II). With dry 8% HCl–Et_2O, (II) gives 1-chloro-1-ethylthiol-*aldehydo-d*-galactose penta-acetate. *d*-Gluco-*d*-guloheptose Et_2 mercaptal hexa-acetate and boiling AcCl give 1-*chloro*-1-*ethylthiol*-aldehydo-d-*gluco-d-guloheptose hexa-acetate*, m.p. 138—139°, $[\alpha]_D^{25}$ +36·7° → −7° in 24 hr. *aldehydo-d*-Glucose penta-acetate, EtSH, Ac_2O, and C_5H_5N give α-1-*ethylthiol*-aldehydo-d-*glucose hexa-acetate* (III), m.p. 101—102°, $[\alpha]_D^{27}$ +12·5°, *aldehydo-d*-glucose hepta-acetate, and, under defined conditions, the *β-isomeride*, m.p. 85—87°, $[\alpha]_D^{23}$ −1·8°, of (III). Treatment of (III) in $CHCl_3$ with, successively, $AlCl_3$ at 0° (then 5°), H_2O, anhyd. $CaSO_4$, MeOH, and Ag_2CO_3–MeOH–anhyd. $CaSO_4$ at room temp., gives d-*glucose* O-*methyl* S-*ethyl monothioacetal penta-acetate*, m.p. 69—71°, $[\alpha]_D^{27}$ +27·1°, hydrolysed by NaOMe–MeOH at room temp. to d-*glucose* O-*methyl* S-*ethyl monothioacetal*, m.p. 116—118°, $[\alpha]_D^{23}$ +47·8° in H_2O. R. S. C.

Stable form of sucrose octa-acetate. R. P. Linstead, A. Rutenberg, W. G. Dauben, and W. L. Evans (*J. Amer. Chem. Soc.*, 1940, **62**, 3260—3263).—Sucrose octa-acetate exists in a form, m.p. 89°, $[\alpha]_D^{25\cdot4}$ +58·5° in abs. EtOH (cryst. form described), which is more stable than the form of m.p. 69—70° and, when once obtained, prevents prep. of the latter. R. S. C.

Preparation of fibrous iodocellulose nitrates. Probable distribution of nitrate groups in partly nitrated celluloses. G. E. Murray and C. B. Purves (*J. Amer. Chem. Soc.*, 1940, **62**, 3194—3197).—Interaction of $·CH_2·O·NO_2$ (in the sugar series) with NaI to give $·CH_2I$ and of $>CH·O·NO_2$ to give $>CH·OH$ is applied to cellulose nitrates, for which the reaction is best effected in a ketone [COMeEt or $(CH_2Ac)_2$]. Guncotton is so highly oxidised as to give invalid results, and less degraded, less nitrated, fibrous products (N 2·5—9·0%) are used. It is tentatively concluded that approx. half the NO_2 introduced are attached to primary C, independently of the degree of nitration. R. S. C.

Starch. XIII. Potato starch. K. H. Meyer, M. Wertheim, and P. Bernfeld (*Helv. Chim. Acta*, 1941, **24**, 378—389).—Warm H_2O removes from potato starch an amylose (I) which is free from P, scarcely sol. in H_2O, and rapidly ages after having been solubilised by alkali and then neutralised in solution. In N_2H_4,H_2O it has almost the same viscosity as maize amylose (II). Methylated (I), like methylated (II), can be drawn into threads and gives resistant films but it has a somewhat greater η. Osmotic measurements indicate ~40,000 for mol. wt. corresponding with a degree of polymerisation ~200. (I) contains 0·4% of terminal groups and is regarded as non-branched. The identity of (I) and (II) is claimed. Treatment of starch with superheated H_2O does not yield amylopectin but gives a degradation product as indicated by the increased Cu no. Similarly erythrogranulose, resistant to the action of β-amylase, is converted by H_2O at 120° into a product degraded by β-amylase. Erythroamylose has a reducing power of 2·3% (expressed as maltose), indicating one free CHO per 90 glucose residues. η of methylated erythroamylose is much inferior to that of non-degraded methylated amylopectin. Potato amylopectin, isolated by repeated extraction of potato starch with H_2O at 70°, contains a small proportion of combined P and has a higher mol. wt. and hence probably a somewhat more branched structure than maize amylopectin. The ability of maize (and rice) starch to crystallise is superior to that of potato starch, the difference being due to constitutional factors, since it persists after dissolution of the sample in $CCl_3·CH(OH)_2$ and repptn. by $COMe_2$, and is attributed to the presence of amylopectins of very high mol. wt. The high η of potato starch solutions appears related to its slight tendency towards crystallisation. The superior size of the granules does not appear important. H. W.

Starch. XIV. Colour reaction of starch and glycogen with iodine. K. H. Meyer and P. Bernfeld (*Helv. Chim. Acta*, 1941, **24**, 389—393).—The reaction between I and starch (I)

involves several mols. of each reactant. Amylose (II) in dil. solution gives a pure blue colour with starch; the solution behaves as an unstable colloid and is flocculated by HCl or Na_2SO_4. The composition of the black-blue ppt. varies from approx. $[I_3(C_6H_{10}O_5)_{10}]_n$ to $[I_2(C_6H_{10}O_5)_{20}]_n$, according to which reactant is in excess. I is not essential for formation of the colour or for flocculation of the compound. H_2O is indispensable; air-dried (I) is coloured by I vapours but the rigorously dried (I) remains colourless. Fractionated (II) which has lost its solubility in H_2O in course of purification is only feebly coloured after desiccation in air. The shade of the solutions varies with (II), potato amylopectin, erythroamyloses, erythrogranuloses, glycogen, and the residual dextrin therefrom from pure blue to yellowish-brown as the carbohydrate mol. becomes more highly branched. It appears to be related also to the tendency towards crystallisation. Purely physical factors are also important. It appears that the blue starch iodide is formed by micelles in the fissures of which I (in presence of H_2O) undergoes a change which displaces its light absorption bands. H. W.

Starch. XII. Arrangement of the glucose residues in glycogen. K. H. Meyer and M. Fuld (*Helv. Chim. Acta*, 1941, **24**, 375—378).—Glycogen contains 9% of terminal groups, indicating one terminal glucose residue for every 11 sugar residues. When treated with pure β-amylase it loses 47% of its wt. as maltose, representing a loss of ~5·5 glucose residues per terminal group. The residual dextrin (53% of the initial material) contains all the terminal groups, thus having one per 5·5 glucose residues. It therefore appears that the exterior branches of the glycogen mol. are formed, as an average, of 7 glucose residues, since 1·5 preserved at the point of ramification and forming the terminal groups of the residual dextrin must be added to the 5·5 residues removed. The glucose residues containing a branching at $C_{(6)}$ can only be separated from one another by very short chains containing, as a mean, 3 glucose residues. The mol. is depicted. H. W.

Optical rotation of aliphatic acid salts of triethylenediaminecobaltic hydroxide. Further evidence for ring structure in aliphatic series. J. P. McReynolds and J. R. Witmeyer (*J. Amer. Chem. Soc.*, 1940, **62**, 3148—3150).—The prep., $[\alpha]_D$, and stability to racemisation of d-*triethylenediaminecobaltic hydroxide* (I) have been studied. $[\alpha]_D$ of the acetate, propionate, butyrate, valerate, hexoate, heptoate, and nonoate of (I) has been determined; the effect of chain length on $[M]_D$ accords with the postulation of a ring structure for ions larger than propionate. W. R. A.

Tetra-alkylmethyleneimmonium salts. H. G. Reiber and T. D. Stewart (*J. Amer. Chem. Soc.*, 1940, **62**, 3026—3030).—$NR_2{\cdot}CR'_2{\cdot}CN$ and $AgNO_3$ in dry EtOH give imine alkiodides, $CR'_2{:}NR_2X$ (*A*). Thus are obtained 20—60% of *β-methyliminopropane methonitrate* (I), decomp. 155—160°, and *methiodide*, *β-methylimino-n-butane methonitrate* and *methiodide*, *γ-methylimino-n-pentane methiodide*, decomp. 140—145°, and *β-methyliminopropane ethiodide* (II), decomp. 195—200°. The salts are hydrolysed to COR'_2 and NHR_2, the reaction being catalysed by NaOH but not by acid. Substitution of Me by Et reduces the rate of hydrolysis, the effect being greater on N than on C. The heat of activation for hydrolysis of (II) is 18,800 g.-cal. per g.-mol. (*A*) may exist partly as $CHR''{:}CR'{\cdot}NR_2X$. Thus, hydrolysis in EtOH by OEt′ or CN′ gives only partial recovery of ketone and amine, probably owing to polymerisation of the vinylamine. KCN and (I) in EtOH yield 37% of $COMe_2$, 72% of $NHMe_2$, and a *salt*, $C_9H_{13}NMe_3I$; in liquid HCN, a base is obtained yielding a *methiodide*, (?) $CN{\cdot}CMe_2{\cdot}NMe_3I$, m.p. 260—265° (decomp.). MgMeI and (II) in Et_2O give, after boiling, NEt_2Bu^{γ} (*platinichloride*, m.p. 223—225°). R. S. C.

3 : 5-Dinitrobenzoyl derivatives of amino-acids and their use in separating isomerides of leucine and valine. B. W. Town (*Biochem. J.*, 1941, **35**, 578—587).—The prep. is described of 3 : 5-*dinitrobenzoyl* derivatives of glycine, m.p. 182·2° (shrinks at 181·4°), *dl*-, m.p. 177°, and *l*(+)-alanine, m.p. 177°, *dl*-valine, m.p. 211·4° (softens at 210·8°), *l*(−)-leucine, m.p. 188° (softens at 187·2°), *l*(+)-*iso*leucine, m.p. 170°, serine, m.p. 183° or (+1H_2O) m.p. 183° after softening at 181° and shrinking at 112°, *l*(−)-threonine, m.p. 181° (softens at 180°), *dl*-phenylalanine, m.p. 161° after softening at 160° (lit. m.p. 93°), glutamic acid, m.p. 182° after softening at 179° (also +1H_2O), aspartic acid, m.p. 184·8° after softening at 184·4° and shrinking at 100° [Na salt (I), m.p. 220°], and β-hydroxyglutamic acid, m.p. 229·5° (decomp.) after darkening at 228°. It is possible to separate the components in mixtures of the various isomerides of valine and leucine by fractional pptn. of their derivatives at differing p_H. (I) can be readily salted out at p_H 4. A derivative of tyrosine could not be obtained. P. G. M.

Preparation of β-alanine methyl ester. H. H. Weinstock, jun., and E. L. May (*J. Amer. Chem. Soc.*, 1940, **62**, 3266).—β-Alanine and CH_2N_2 in Et_2O containing a little H_2O give 67% of Me ester, b.p. 54—55°/13 mm., the purity of which is estimated by the m.p. of the platinichloride [(pure) 193°]. R. S. C.

***p*-Nitro- and *p*-amino-benzoyl-*d*-(−)-glutamic acid.** H. C. Winter (*J. Amer. Chem. Soc.*, 1940, **62**, 3266—3267).—Resolution of the *dl*-acid by strychnine in H_2O gives p-*nitro*-, softens at 77°, m.p. 115—116°, $[\alpha]$ −160·02° in aq. alkali (2 mols.), and thence p-*amino-benzoyl*-d-(−)-*glutamic acid*, m.p. 166—167° (lit. 175°), $[\alpha]$ −27·4° in aq. alkali (2 mols.), +15·5° in 9% HCl. R. S. C.

Anodic reaction and waves of cysteine at the dropping mercury electrode and at the platinum micro-wire electrode. I. M. Kolthoff and C. Barnum (*J. Amer. Chem. Soc.*, 1940, **62**, 3061—3065).—Cysteine (I) can be determined polarographically at the dropping Hg electrode in 0·1M-$HClO_4$. The half wave potential at p_H = 1 is −0·05 v. (relative to the saturated calomel electrode) and independent of the concn. of (I). The diffusion current is ∝ the concn. of (I) and the diffusion coeff. is calc. as $3{\cdot}10 \times 10^{-5}$ cm.² per sec. at 25°. Current–voltage curves at p_H 1, 2, 4, 5, 6, and 9·2 are given. From p_H 2 to 6 the anodic waves are quite irregular, a low false diffusion current being obtained over a wide range of potential. The abnormality is attributed to the formation of a film of Hg^I cysteinate (II) around the Hg drop. At p_H 1 and 9·2 the irregularity is greatly reduced, probably owing to the solubility of (II) in strongly acid and alkaline media. At the Pt micro-wire electrode the anodic waves of (I) occurred at ~0·6 v. more positive than at the Hg electrode and correspond with the formation of cystine, whilst at the Hg electrode the anodic waves are attributed to the formation of (II). At $[Hg^{\cdot}]$ $\sim 10^{-20}$M. practically all Hg^I is present in solution as $Hg^{\cdot}$ and not as $Hg_2^{\cdot\cdot}$. W. R. A.

Structure of acet-*d*-glucosylamide. C. Niemann and J. T. Hays (*J. Amer. Chem. Soc.*, 1940, **62**, 2960—2961).—The Ac derivative, m.p. 255°, $[\alpha]_D^{22}$ −22·4° in H_2O, obtained by condensing glucose with NH_3 and treating the product with keten in 91% MeOH at 0° (cf. Bergmann *et al.*, A., 1930, 459), is acet-α- or -β-*d*-glucopyranosylamide. With Ac_2O–C_5H_5N at 25° it gives a penta-acetate, new m.p. 160—161°, $[\alpha]_D^{22}$ +171·7° in $CHCl_3$. It consumes 2 HIO_4 and when subsequently treated with Br–$BaCO_3$ gives acetamido-*D*-hydroxymethyldiglycollic acid (*Ba*, $[\alpha]_D^{22}$ +24±2° in H_2O, and *brucine* salt). R. S. C.

So-called benzenesulphonylguanidine and similar compounds. P. Karrer and A. Epprecht (*Helv. Chim. Acta*, 1941, **24**, 310—311).—The product of the action of $PhSO_2Cl$ on an alkaline guanidine (I) solution is not benzenesulphonylguanidine but *guanidine benzenesulphonate*, also obtained from (I) and $PhSO_3H$. Similarly (I) and *p*-$NO_2{\cdot}C_6H_4{\cdot}SO_2Cl$ or *p*-$NO_2{\cdot}C_6H_4{\cdot}SO_3H$ afford *guanidine* p-*nitrobenzenesulphonate*, m.p. 250—252°, reduced to *guanidine* p-*aminobenzenesulphonate*, m.p. 216°. H. W.

Additive compounds formed in the desulphurisation of thiocarbamides by copper hydroxide. W. M. Dehn (*J. Amer. Chem. Soc.*, 1940, **62**, 3189—3190).—Cone. Fehling's solution and thiocarbamides give isolable additive compounds. Thiocarbamides NHR·CS·NHR′ (I) give (I)–$Cu(OH)_2$ (anhyd. or monohydrate), whilst NHR·CS·NR′R″ (II) yield $(II)_2$–$Cu(OH)_2$. Compounds (I)–$Cu(OH)_2$ fairly readily lose H_2O and then decompose to H_2O, CuS, and carbodi-imides. Compounds $(II)_2$–$Cu(OH)_2$ do not readily give CuS. W. R. A.

B.p. of *n*-alkyl nitriles.—See A., 1941, I, 295.

Utilisation of the alcoholates of azidoalcohols for synthesis of azido-derivatives of ethers. I. Alcoholate of azidoethanol and its application for the synthesis of azido-derivatives of ethers. K. A. Kornev and S. B. Serebriani (*Ber. Inst. Chem. Akad. Wiss. Ukrain.*, 1940, **6**, 343—351).—$N_3{\cdot}[CH_2]_2{\cdot}OH$ is decomposed by Na without a solvent but gives the *alkoxide*

in Et_2O. In Et_2O with EtI this gives β-azidoethyl ether, b.p. 49—50°/25 mm., which is decomposed by $SnCl_2$ + HCl; with allyl bromide it gives β-azidoethyl allyl ether, b.p. 63—64°/25 mm., which polymerises on keeping and is decomposed by $SnCl_2$ + HCl. J. J. B.

Synthesis and physiological properties of ββ′-dichlorodivinylcyanoarsine. S. T. Li (*J. Chinese Chem. Soc.*, 1940, **7**, 117—120).—The prep. of Lewisites I, II, and III, b.p. 84°/12 mm., 110°/12 mm., and 127—136°/12 mm., respectively, is described. Lewisite II with aq. KCN yields cryst. ββ′-cyanodichlorodivinylarsine, b.p. (impure) 120°/12 mm. A small drop of this on the skin of a rat causes death in 2 hr., but has no observable effect on the heart. A. Li.

II.—HOMOCYCLIC.

Carotenoids in corn gluten. D. Nagy (*Iowa State Coll. J. Sci.*, 1940, **15**, 89—92; cf. Kuhn and Grundmann, A., 1934, 703; Buxton, A., 1939, III, 639).—Zeaxanthin (**I**) from *Physalis alkekengi* when heated in C_6H_6 yields neozeaxanthin-*A* and -*B*, m.p. 108—109° (absorption max. at 480 and 453 mμ). Heating with dil. AcOH forms a small amount of the -*A* isomeride; with dil. HCl, in addition to the -*A* and -*B* isomerides, cryptoxanthin (?) and several unidentified pigments are formed. (**I**) in C_6H_6–EtOH with O_2 at room temp. for 2 days gives a little of the -*A* and -*B* isomerides and two unidentified oxidation products. The pigments in the colouring matters obtained from corn under various conditions are those resulting from the action of acids or heat on (**I**). J. L. D.

Alkylation of benzene with *d*-*sec*.-butyl alcohol. C. C. Price and M. Lund (*J. Amer. Chem. Soc.*, 1940, **62**, 3105—3107).—C_6H_6 and *dl*-CHMeEt·OH with BF_3 or $AlCl_3$ gives 50—60% of *dl*-CHPhMeEt. *d*-CHMeEt·OH, $[\alpha]_D^{20}$ +11·05° to +11·46°, and C_6H_6–BF_3 give CHPhMeEt, $[\alpha]_D^{20}$ −0·15° to −0·16°, but with $AlCl_3$ gives the *dl*-compound. R. S. C.

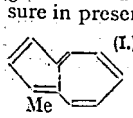
Isomerisation accompanying alkylation. III. Alkylation of benzene with neopentyl chloride and alcohol. H. Pines, L. Schmerling, and V. N. Ipatiev (*J. Amer. Chem. Soc.*, 1940, **62**, 2901—2902; cf. A., 1940, II, 247).—Formation of $CPhMe_2Et$ (~30%) from $CH_2Bu^{\gamma}·OH$, C_6H_6, and 80% H_2SO_4 at 65° provides the first change of C skeleton observed during alkylation of an aromatic compound. However, in presence of $AlCl_3$ at 0° and later at the b.p., CH_2PhBu^{γ} (9%) is obtained. $CH_2Bu^{\gamma}Cl$, C_6H_6, and $AlCl_3$ at 0° give $CHPhMePr^{\beta}$ (~24%), probably by way of $CH_2{:}CHPr^{\beta}$. R. S. C.

Reactions of unsaturated nitro-compounds derived from terephthalaldehyde. D. E. Worrall (*J. Amer. Chem. Soc.*, 1940, **62**, 3253—3254).—*p*-$C_6H_4(CH{:}CH·NO_2)_2$ (**I**) gives a tetrabromide, m.p. 190—191°, which with warm KOAc–AcOH gives p-*di*-(*β-bromo-β-nitrovinyl*)*benzene* (**II**), m.p. 169—170°. With fuming HNO_3, (**I**) gives 2-*nitro*-1 : 4-*di*-(*β-nitrovinyl*)*benzene*, m.p. 173—174°. (**II**) is converted by cold KOH–MeOH, followed by Br–H_2O, into p-*di*-(*ββ-dibromo-β-nitro-α-methoxyethyl*)*benzene*, m.p. 215—216° (decomp. from 210°), and with boiling KOH–MeOH, followed by AcOH containing a little H_2SO_4, gives p-*di*-(*β-nitroacetyl*)*benzene*, m.p. ~190° (decomp.). NH_2Ph and (**I**) at 100° give p-*di*-(*β-nitro-α-anilinocthyl*)*benzene*, m.p. 157—158° (decomp.), which gives salts with acid and alkali, and with NH_3 gives an amorphous polymeride, m.p. >300°, of (**I**) with a small amount of cryst. (?) additive product. *p*-$C_6H_4(CHO)_2$ (**III**) and $EtNO_2$ with NEt_3 (not NH_2R) give p-*di*-(*β-nitropropenyl*)*benzene* (poor yield), m.p. 119—120°. $CH_2Ph·NO_2$, (**I**), and $C_5H_{11}·NH_2$ give p-*di*-(*β-nitro-β-phenylvinyl*)*benzene* (**IV**), m.p. 228—229° (decomp.). $CH_2Ph·NO_2$, (**IV**), and NH_3 in warm EtOH give p-*di*-(2-*oxido*-3 : 5-*diphenylisooxazolyl*)*benzene*, m.p. 253—254° (decomp.), converted in hot $PhNO_2$ into p-*di*-(3 : 5-*diphenylisooxazolyl*)*benzene*, m.p. 316—317°. *p*-$C_6H_4Br·CH_2·NO_2$ (**V**), (**IV**), and NH_3 in warm EtOH give p-*di*-(2-*oxido*-3-*phenyl*-5-p-*bromophenylisooxazolyl*)*benzene*, m.p. 229—230° (decomp.), which in hot $PhNO_2$ gives p-*di*-(3-*phenyl*-5-p-*bromophenylisooxazolyl*)*benzene*, m.p. 298—299°. (**I**) and (**V**) give p-*di*-(*β-nitro-β*-p-*bromophenylvinyl*)*benzene*, m.p. 222—223° (decomp.), and thence the *iso*oxazole derivative, m.p. 323—324° (decomp. from 290°) [oxide, m.p. 248—249° (decomp.)]. R. S. C.

Tetrachloronaphthalenes derived from dichloronaphthalene tetrachlorides and from trichloronaphthalenesulphonic acids. (Miss) E. G. Turner and W. P. Wynne (*J.C.S.*, 1941, 243—257; cf. *Proc. C.S.*, 1890, 76).—1-$C_{10}H_7Cl$ and Cl_2 give 1-chloronaphthalene tetrachloride (**I**), m.p. 131—132° (6 parts), and 1 : 4-$C_{10}H_6Cl_2$ (1 part), with an uncrystallisable syrup; the use of light petroleum as solvent gives a similar result, but lower yields, and the use of $CHCl_3$ affords (**I**) and (mainly) 1 : 4-dichloronaphthalene tetrachloride (**II**) (22% yield), m.p. 172°, identical with that prepared by Widman (*Bull. Soc. chim.*, 1878, **28**, 506). 1-$C_{10}H_7Cl$ and Cl_2 in CS_2 give a *dichloronaphthalene tetrachloride* (**III**), m.p. 158°; this experiment is difficult to repeat, giving usually much (**I**), (**II**), and/or 1 : 4-$C_{10}H_6Cl_2$, and (**III**) is best obtained by introducing Cl_2 into (**I**) in CS_2 in bright sunlight (HCl and S_2Cl_2 are evolved). (**II**) is heteronucleal. (**II**) and NaOEt–EtOH afford 1 : 3 : 5 : 8-*tetrachloronaphthalene* (**IV**), m.p. 131°, converted by $ClSO_3H$–CS_2 into a sulphonic acid (*Na* salt, +H_2O; the *chloride*, m.p. 146°, and PCl_5 at 198—215° afford a *pentachloronaphthalene*, m.p. 155°). (**II**) heated at 330—356° gives 2 : 3 : 5 : 8-*tetrachloronaphthalene* (**V**), m.p. 133—136° or 139°. (**V**) and $ClSO_3H$ (2 mols.) in CS_2 afford a sulphonic acid; its *chloride* (**VI**), m.p. 133°, gives the *Na* salt (+H_2O), which in H_3PO_4 (*d* 1·75) is hydrolysed with steam at 240—250° to (**V**). (**VI**) and PCl_5 at 180—190° give 2 : 3 : 5 : 8 : x-*pentachloronaphthalene*, m.p. 131°. (**III**) (m.p. 157°) and NaOEt–EtOH give 1 : x : x : x-*tetrachloronaphthalene*, m.p. 196°, converted by 5% oleum at 150° into a sulphonic acid which affords two *chlorides*, (*a*) m.p. 132° (anhyd.) or ~107—122° (+C_6H_6) (hydrolysed to *Na tetrachloronaphthalenesulphonate*, converted by PCl_5 at 192—208° into a *pentachloronaphthalene*, m.p. 147°), and (*b*) m.p. 199—200°. The 14 isomeric $C_{10}H_5Cl_3$ and $ClSO_3H$ (slight excess of 1 mol.) in CS_2 give sulphonic acids, converted into the respective Ba and Na salts, chlorides, and thence by PCl_5 (~180—210°) into the corresponding $C_{10}H_4Cl_4$. 15 of the 22 possible $C_{10}H_4Cl_4$ are described and constitutions are definitely assigned to 7 of them. Thus, 1 : 2 : 3-$C_{10}H_5Cl_3$, m.p. 80·5° [from (**I**)–NaOEt–EtOH], affords the 5- (mainly) (*Na* salt, +H_2O; *amide*, m.p. 249°) and 7-sulphonic acid (*Na* salt, +H_2O; *amide*, m.p. 245°), separable through the chlorides. 1 : 2 : 3-*Trichloronaphthalene*-5-*sulphonyl chloride* has m.p. 131° [the product, m.p. 182°, described previously (*loc. cit.*) as mono- is the 5 : 7-*di-sulphonyl chloride* (**VII**), new m.p. 184°] and with an equal wt. of PCl_5 at 178—181° yields 1 : 2 : 3 : 5-*tetrachloronaphthalene*, m.p. 141°, which with $ClSO_3H$–CS_2 gives the 7-sulphonic acid (*Na* salt, +1·5H_2O) and thence the 7-*sulphonyl chloride* (**VIII**), m.p. 176° [converted by PCl_5 at 203—210° into 1 : 2 : 3 : 5 : 7-*pentachloronaphthalene* (**IX**), m.p. 171°], and a product, m.p. 132—134°. 1 : 2 : 3 : 7-$C_{10}H_4Cl_3·SO_2Cl$, m.p. 157°, and PCl_5 at 187—192° give 1 : 2 : 3 : 7-*tetrachloronaphthalene*, m.p. 115°, converted by $ClSO_3H$ into an acid (*Na* salt, +2H_2O) which affords mainly the 5-chloride, m.p. 199° (and a little of a chloride, m.p. 154—155°), which with PCl_5 at 213—220° gives (**IX**). 1 : 2 : 3-$C_{10}H_5Cl_3$ and 10% oleum at 100° afford the 5 : 7-disulphonic acid (*K* salt, +3H_2O; *Ba* salt, +4H_2O); the corresponding chloride (**VII**) with PCl_5 at 183—188° affords (**IX**) and (after treating with KOH–EtOH) *K* 1 : 2 : 3 : 5-*tetrachloronaphthalene*-7-*sulphonate* (+H_2O) (*Ba* salt; *amide*, m.p. 235°), which is hydrolysed to 1 : 2 : 3 : 5-$C_{10}H_4Cl_4$ or is converted by PCl_5 into (**VIII**). 1 : 2 : 4-$C_{10}H_5Cl_3$, m.p. 92° (from 2 : 4 : 1-$C_{10}H_5Cl_2·NH_2$), and $ClSO_3H$–CS_2 yield an acid and thence *sulphonyl chlorides*, m.p. 158° and 124—129°. The former and PCl_5 at 185—198° give 1 : 2 : 4 : 6-*tetrachloronaphthalene* (**X**), m.p. 111°. Sulphonation with 10% oleum at 150° then gives a sulphonic acid [*Na* salt, +1·5H_2O, is hydrolysed to (**X**)], the *chloride*, m.p. 140°, of which with PCl_5 at 190—202° affords 1 : 2 : 4 : 6 : x-*pentachloronaphthalene*, m.p. 135°. 1 : 2 : 5-$C_{10}H_5Cl_3$, m.p. 79° (from 2 : 1 : 5-$NH_2·C_{10}H_5Cl·SO_3H$), is sulphonated by $ClSO_3H$ to give two *sulphonic acids*, (*a*) (*K* salt; *Na* salt, +H_2O; *chloride*, m.p. 146°, and PCl_5 at 185—195° give 1 : 2 : 5 : x-*tetrachloronaphthalene*, m.p. 164°) and (*b*) (*K* salt, +H_2O; *Na* salt, +1·5H_2O; *chloride*, m.p. 179°, gives 1 : 2 : 5 : x-*tetrachloronaphthalene*, m.p. 114°, and after solidifying at ~98°, has m.p. 110°) 1 : 2 : 6-$C_{10}H_5Cl_3$, m.p. 92° (from 2 : 1 : 6-$NH_2·C_{10}H_5Cl·SO_3H$), yields the 4-sulphonic acid [*Na* salt, +2H_2O; 4-*sulphonyl chloride*, m.p. 184°, and PCl_5 at 195—202° yield (**X**)]. 1 : 2 : 7-$C_{10}H_5Cl_3$, m.p. 84° or 88° (from 2 : 1 : 7-$NH_2·C_{10}H_5Cl·SO_3H$), affords a sulphonic acid (*K*, +H_2O, *Na*, +H_2O, and *Ba* salt, +3·5H_2O; *chloride*, m.p. 176°, and PCl_5 at 185—195° give 1 : 2 : 7 : x-*tetrachloronaphthalene*, m.p. 144°). 1 : 2 : 8-$C_{10}H_5Cl_3$, m.p. 84° (from 1 : 2 : 8-$C_{10}H_5Cl_2·SO_2Cl$), yields a sulphonic acid (*K* and *Ba*

salt, $+H_2O$), the *chloride*, m.p. 105°, of which with PCl_5 at 188—205° gives 1 : 2 : 8 : x-*tetrachloronaphthalene*, m.p. 135°. 1 : 3 : 5-$C_{10}H_5Cl_3$, m.p. 103°, and $ClSO_3H$–CS_2 give the *sulphone*, $C_{20}H_8O_2Cl_6S$, m.p. 305°, and the 7-sulphonic acid [*K* and *Ba* salt, $+2{\cdot}5H_2O$; *chloride*, m.p. 152°, converted by PCl_5 at 197—206° into 1 : 3 : 5 : 7-*tetrachloronaphthalene* (**XI**), m.p. 179°]. 1 : 3 : 6-$C_{10}H_5Cl_3$, m.p. 80·5° [from 1 : 3 : 6-$NO_2{\cdot}C_{10}H_5(SO_2Cl)_2$], gives the sulphonic acid (*K*, $+H_2O$, *Na*, $+1{\cdot}5H_2O$, and *Ba* salt), of which the *chloride*, m.p. 156°, and PCl_5 give 1 : 3 : 6 : 7-*tetrachloronaphthalene* (**XII**), m.p. 119—120° (NO_2-derivative, m.p. 145°). 1 : 3 : 7-$C_{10}H_5Cl_3$, m.p. 113° [from 2 : 6 : 8-$C_{10}H_5Cl(SO_2Cl)_2$], yields much sulphone and the 5-acid (*K*, $+0{\cdot}5H_2O$, *Na*, $+2{\cdot}5H_2O$, and *Ba* salt, $+3{\cdot}5H_2O$) and thence the 5-*sulphonyl chloride*, m.p. 138°, and (PCl_5 at 188—195°) (**XI**). 1 : 3 : 8-$C_{10}H_5Cl_3$, m.p. 89·5° and 84° [from 1 : 3 : 8-$C_{10}H_5Cl(SO_2Cl)_2$], and $ClSO_3H$ yield the 5-sulphonic acid (*K*, $+1{\cdot}5H_2O$, *Na*, $+1{\cdot}5H_2O$, and *Ba* salt, $+3H_2O$); the *chloride*, m.p. 127°, and PCl_5 at 172—185° afford (**IV**). 1 : 4 : 7-$C_{10}H_5Cl_3$, m.p. 68° [obtained from 1 : 7 : 4-$C_{10}H_5Cl_2{\cdot}SO_2Cl$, m.p. 119° ($+C_6H_6$)], affords a sulphonic acid (*K*, $+H_2O$, *Na*, $+H_2O$, and *Ba* salt) and the *chloride*, m.p. 144°, and PCl_5 at 190—195° yields 1 : 4 : 7 : x-*tetrachloronaphthalene*, m.p. 109°. 1 : 4 : 8-$C_{10}H_5Cl(SO_2Cl)_2$ (**XIII**) and PCl_5 at 160—170° give much $C_{10}H_5Cl_2{\cdot}SO_3H$, separated through the *Ba* salts (one anhyd. and one, $+2H_2O$) to give *Na* 1 : 8-*dichloronaphthalene*-4- ($+0{\cdot}5H_2O$) (*chloride*, m.p. 117°, yields 1 : 4 : 8-$C_{10}H_5Cl_3$) and -8-*sulphonic acid* (*chloride*, m.p. 96°, gives 1 : 4 : 8-$C_{10}H_5Cl_3$), respectively. (**XIII**) and PCl_5 (3 mols.) at 195—215° yield 1 : 4 : 8-$C_{10}H_5Cl_3$, sulphonated ($ClSO_3H$) to a Na sulphonate and thence two *chlorides*, m.p. 118° (6-chloride) (derived *Na* salt, $+1{\cdot}25H_2O$), and m.p. 178° (*Na* salt, $+1{\cdot}5H_2O$), converted by PCl_5 at 180—210° into (**IV**) or 1 : 4 : 8 : x-*tetrachloronaphthalene*, m.p. 144°, respectively. 2 : 3 : 5-$C_{10}H_5Cl_3$, m.p. 109° (from 2 : 3 : 5-$C_{10}H_5Cl_2{\cdot}SO_2Cl$), is sulphonated to an acid (*K*, $+H_2O$, and *Ba* salt, $+3H_2O$), the *chloride*, m.p. 164°, of which affords (**V**). 2 : 7-$C_{10}H_6Cl_2$ and $ClSO_3H$ give 2 : 7-*dichloronaphthalene*-3-, m.p. 166°, and -4-*sulphonyl chloride*, m.p. 152° (convertible into 1 : 3 : 6-$C_{10}H_5Cl_3$). 2 : 3 : 6-$C_{10}H_5Cl(SO_2Cl)_2$ and PCl_5 at 195—207° give 2 : 3 : 6-$C_{10}H_5Cl_3$ and a little of *Na* 2 : 6-*dichloronaphthalene*-3-*sulphonate*, $+5H_2O$ (hydrolysed by HCl at 260° to 2 : 6-$C_{10}H_6Cl_2$) (*chloride*, m.p. 131°). 2 : 3 : 6-$C_{10}H_5Cl_3$ and $ClSO_3H$ afford, through the Ba and Na salts, two *sulphonyl chlorides*, m.p. 118° (8-) (corresponding *Na* salt, $+1{\cdot}5H_2O$; *Ba* salt, $+3{\cdot}5H_2O$) and 94° (*Na* salt, $+H_2O$; *Ba* salt, $+3H_2O$), converted by PCl_5 at 190—210° or 180—190°, respectively, into (**XII**) or 2 : 3 : 6 : x-*tetrachloronaphthalene*, m.p. 218°. Although the main product of the sulphonation of 1 : 5-$C_{10}H_6Cl_2$ is the 3-sulphonic acid, some 1 : 5 : 2-$C_{10}H_5Cl_2{\cdot}SO_2Cl$, m.p. 125°, is also obtained, which with PCl_5 at 190—192° affords 1 : 2 : 5-$C_{10}H_5Cl_3$. 1 : 5 : 2-$C_{10}H_5Cl_2{\cdot}SO_3Na$, $+H_2O$, is hydrolysed by superheated steam to 1 : 5-$C_{10}H_6Cl_2$. A. T. P.

Sesquiterpenes. XLVII. Synthesis of mono- and dimethylazulenes. P. A. Plattner and J. Wyss (*Helv. Chim. Acta*, 1941, **24**, 483—492).—$CHN_2{\cdot}CO_2Et$ is slowly added to 1-methylindane at 135° and the mixture is heated to 165° and hydrolysed. The crude acid is simultaneously dehydrogenated and decarboxylated by distillation under atm. pressure in presence of Pd–C, thus giving a poor yield of 1-*methylazulene* (**I**) as a dark blue liquid which gives a *picrate*, m.p. 134—135°, and an additive *compound*, m.p. 160—161°, with $C_6H_3(NO_2)_3$. COPhEt is condensed with paraformaldehyde by K_2CO_3 in MeOH to $CHMeBz{\cdot}CH_2{\cdot}OH$, which is cyclised by conc. H_2SO_4 to 2-methylindan-1-one (**II**), reduced (Clemmensen) to 2-methylindane, b.p. 69°/10 mm. This is transformed by the method used for (**I**) into 2-*methylazulene* (**VI**), m.p. 47—48° [*picrate*, m.p. 130—131°; additive *compound*, m.p. 140—141°, with $C_6H_3(NO_2)_3$]. The absorption spectrum of (**III**) differs markedly from that of (**I**), guaiazulene, and azulene but shows certain analogies with that of vetivazulene; the Me at $C_{(2)}$ appears to exert a sp. influence. (**II**) is treated with MgMeI and the product is distilled with $KHSO_4$ and then hydrogenated (Raney Ni) to 1 : 2-*dimethylindane*, b.p. 79—80°/10 mm. This is transformed by the usual processes into 1 : 2-*dimethylazulene*, m.p. 58—59° [*picrate*, m.p. 129—130°; additive compound with $C_6H_3(NO_2)_3$, m.p. 166—167°]. 2 : 5 : 1-$C_6H_3Me_2{\cdot}CH_2Cl$ is condensed with $CHNa(CO_2Et)_2$ in boiling xylene to a product, b.p. 139—141°/~1 mm., which is directly hydrolysed and decarboxylated to *β*-p-*xylylpropionic acid*, b.p. 165—178°/10 mm., m.p. 45—46°. The corresponding chloride, b.p. 127—128°/10 mm., is cyclised by $AlCl_3$ in light petroleum to 4 : 7-dimethylindan-1-one, b.p. 135—137°/10 mm., m.p. 78—79°, reduced (Clemmensen) to 4 : 7-dimethylindane, b.p. 94—97°/10 mm. This is converted by aid of $CHN_2{\cdot}CO_2Et$ into 4 : 8-dimethylazulene, m.p. 69—70° [*picrate*, m.p. 157—158°; additive *compounds*, m.p. 179—180°, with $C_6H_3(NO_2)_3$], probably identical with the hydrocarbon derived from *β*-vetivone. H. W.



(I.)

Preparation of alkylidenefluorenes from fluorene and aliphatic aldehydes. R. F. Schultz and C. F. Smullin (*J. Amer. Chem. Soc.*, 1940, **62**, 2904—2905).—Addition of fluorene and then of aliphatic RCHO to KOEt in xylene gives 9-propylidene- (*dibromide*, m.p. 102—103°), -*iso*butylidene- (*dibromide*, m.p. 131—132°), and -n-*butylidene-fluorene*, m.p. 55° [*dibromide*, m.p. 93—94° (decomp.)]. Zn–AcOH–EtOH converts the dibromide into impure oils. R. S. C.

Synthesis of 9 : 10-dimethyl-1 : 2-benzanthracene and of a thiophen isologue. R. B. Sandin and L. F. Fieser (*J. Amer. Chem. Soc.*, 1940, **62**, 3098—3105).—1 : 2-$C_{10}H_6(CO)_2O$ and Mg 2-thienyl iodide in boiling Et_2O–C_6H_6–N_2 give 1-*carboxy*-2-*naphthyl* (**I**) (28%), m.p. 158—159·5° (decarboxylation with basic Cu carbonate gives *β*-$C_{10}H_7$ 2-thienyl ketone), and 2-*carboxy*-1-*naphthyl* 2-*thienyl ketone* (**II**) (16%), m.p. 220—221° (separated as Na salt; decarboxylation gives an oil). MgMeBr and (**I**) give (66%) 2-*α*-*hydroxy*-*α*-2′-*thienylethyl* 1-*naphtholactone*, m.p. 112—113°, reduced by Zn–HCl to 2-*α*-2′-*thienylethyl*-1-*naphthoic acid*, m.p. 132—134°. Cyclisation by $ZnCl_2$–Ac_2O–AcOH then gives 4-*acetoxy*-9-*methyl*-5 : 6-*benzthiophanthrene* [4-*acetoxy*-1-*methylthiopheno*-2′ : 3′-2 : 3-*phenanthrene*], m.p. 186—187°, which cannot be reduced (only a product, m.p. ~260—270°, was obtained), does not exchange the OAc for Me by Grignard cleavage, but with $K_2Cr_2O_7$ in boiling AcOH gives 5 : 6-*benz*-4 : 9-*thiophanthraquinone* (**III**) (very low yield), m.p. 166·5—167°. P_2O_5 in $PhNO_2$ at 160—165° converts (**I**) or (**II**) or mixtures thereof into mixed quinones (*A*), m.p. 178—180°, whence (**III**) and a quinone (? impure 5 : 6-benzthiophanthra-4 : 9-quinone [thiopheno-2′ : 3′-3 : 2-phenanthra-1 : 4-quinone]) (**IV**), m.p. 199—201°, are isolated. 1 : 2-Benzanthraquinone treated with MgMeI in Et_2O–C_6H_6 first at room temp. and then at 5°, poured into (best) HI–MeOH, and finally treated with AcOH, gives 70% of 9-*methyl*-10-*iodomethyl*-1 : 2-*benzanthracene* (**V**), decomp. 99°. (**V**) is also obtained from 9-methyl-1 : 2-benzanthracene by $CH_2Cl{\cdot}OMe$, followed by HI (*d* 1·7), in AcOH at 0°; its structure is proved by its spectrum; with NaOR–ROH it gives 9-*methyl*-10-*methoxy*-, m.p. 120—121°, and -10-*ethoxy*-, m.p. 126—127°, -*methyl*-1 : 2-*benzanthracene*; it is reduced by $SnCl_2$–HCl in boiling dioxan to 9 : 10-dimethyl-1 : 2-benzanthracene (99%) [peroxide, m.p. 194—195° (decomp.), formed rapidly in presence of Al_2O_3], which is best thus prepared. Interaction of MgMeI with (*A*) or (**V**) and treatment as above gives 4 : 9-*dimethyl*-, m.p. 158—159°, and under other conditions (?) 4-*methyl*-9-*methoxymethyl*-5 : 6-*benzthiophanthrene*, m.p. 121—122°. M.p. are corr. R. S. C.

Aromatic cyclodehydration. VIII. 6-Methyl- and 5-methyl-6-ethyl-chrysene. C. K. Bradsher and A. S. Burhans (*J. Amer. Chem. Soc.*, 1940, **62**, 3140—3141; cf. A., 1941, II, 8).—*β*-$C_{10}H_7{\cdot}C_6H_4{\cdot}CO_2Me$-*o* (**I**), m.p. 63°, and MgMeI give an oily carbinol, converted by distillation at 18 mm. into 11 : 11-*dimethylchrysofluorene* (56%), m.p. 148—148·5°, but by $KHSO_4$ at 160° into 2-*o*-*iso*propenylphenylnaphthalene (47%), b.p. 180—185°/4 mm., which by treatment with *p*-$CO_2H{\cdot}C_6H_4{\cdot}CO_3H$ and then boiling 40% HBr and AcOH gives 6-methylchrysene (13% calc. on the acid). MgEtI and (**I**) give similarly (?) 5-*methyl*-6-*ethylchrysene* (24%), m.p. 125·5—126·5° (*picrate*, m.p. 94·5—95·5°). R. S. C.

Synthesis of 3 : 4-benzphenanthrene and 1-methylpyrene. W. E. Bachmann and R. O. Edgerton (*J. Amer. Chem. Soc.*, 1940, **62**, 2970—2973).—4-Keto-1 : 2 : 3 : 4-tetrahydrophenanthrene, $CH_2Br{\cdot}CO_2Me$, Zn, and a little I in C_6H_6–Et_2O give *Me* 1 : 2-*dihydro*-4-*phenanthrylacetate*, b.p. 220—225°/1·5 mm., reduced by Na–MeOH to *β*-1 : 2 : 3 : 4-tetrahydro-4-phenanthrylethyl alcohol (impure), b.p. 230—235°/0·9 mm. The derived (PBr_3–C_6H_6) impure bromide, b.p. 185—195°/0·8 mm., is condensed with $CH_2(CO_2Et)_2$ by NaOEt–EtOH, hydrolysed (45% KOH), decarboxylated (160—180°), esterified (CH_2N_2), dehydrogenated (Pd–C; 240—260°), and hydro-

lysed (45% KOH), yielding *γ*-4-*phenanthryl*-n-*butyric acid*, m.p. 139·5—141°. With $SOCl_2$ and a drop of C_5H_5N in Et_2O at room temp., followed by $SnCl_4$ in C_6H_6, this gives 1′-*keto*-1′ : 2′ : 3′ : 4′-*tetrahydro*-3 : 4-*benzphenanthrene*, m.p. 126·5—127·5°, reduced by Zn–Hg–HCl–AcOH–PhMe to 1′ : 2′ : 3′ : 4′-*tetrahydro*-3 : 4-*benzphenanthrene*, m.p. 91—93° (*picrate*, m.p. 118—119°), which with Pd–C at 310—320° gives 3 : 4-benzphenanthrene, m.p. 67·5—68·3° [lit. 68°, 65·6—66·2° (corr.)] (picrate, new m.p. 128—128·5°). $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ and a little $HgCl_2$ and CCl_4 reduce 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (**I**) to 4-*hydroxy*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (85—96%), m.p. 130·5—132° (the 1-OH-is similarly obtained from the 1-CO· compound), which with HCl–$CaCl_2$ in C_6H_6 gives the 4-*Cl*-compound, m.p. 75—77° (decomp.). Condensation thereof with $CHNa(CO_2Et)_2$ in C_6H_6, hydrolysis, and decarboxylation (as above) yields 1 : 2 : 3 : 4-*tetrahydro*-4-*phenanthrylacetic acid* (44%), m.p. 140—141°, which gives (as above) 1-*keto*-1 : 2 : 2a : 3 : 4 : 5-*hexahydropyrene*, m.p. 124—125·5°, 1 : 2 : 2a : 3 : 4 : 5-hexahydropyrene, m.p. 104·5—106° (picrate, new m.p. 148·5—150°), and pyrene. MgMeI and (**I**) in Et_2O–C_6H_6 give a carbinol, converted by Pd–C at 300—320° into 1-*methylpyrene*, m.p. 147·5—148·5° (*picrate*, m.p. 226—227°).

R. S. C.

Retention of asymmetry during the Curtius and the Beckmann change. J. Kenyon and D. P. Young (*J.C.S.*, 1941, 263—267; cf. A., 1939, II, 308).—Curtius rearrangement of the azide of (+)-hydratropic acid gives (−)-*α*-phenylethylamine, of 99·3% optical purity. Probably no racemisation occurs during migration of the optically active ·CHMePh group; the loss of 0·7% is probably due to experimental error. The previously observed loss of 4·2% in optical purity during the analogous Hofmann rearrangement (*loc. cit.*) may be connected with the known racemisation of carbimides by alkalis. The bromide (prep. by PBr_3), b.p. 97—98°/15 mm., $[\alpha]^{20}_{5461}$ −1·2° in Et_2O (the dl-*bromide* has b.p. 97°/19 mm.), of *l*(−)-CHEtBu$^{\alpha}$·CO_2H (amide, m.p. 98°, $[\alpha]^{20}_{5461}$ −3·9° in EtOH) and $CdMe_2$ in Et_2O afford l(−)-*Me γ-heptyl ketone*, b.p. 63—64°/9 mm., $[\alpha]^{21}_{5461}$ −0·9° in EtOH (the *dl*-ketone has b.p. 73°/15 mm., 176—179°/760 mm.). The *l*-ketone gives *l*(+)-Me *anti*-*γ*-heptyl ketoxime, b.p. 111—113°/12 mm., $[\alpha]^{20}_{5461}$ +0·3° in Et_2O, which undergoes Beckmann transformation (PCl_5 in Et_2O) into l(+)-*acet*-*γ*-*heptylamide*, m.p. 43—44·5°, $[\alpha]^{21}_{5461}$ +1·4° in EtOH. *dl*-CHEtBu$^{\alpha}$·$CO·NH_2$ and Br–aq. NaOH yield dl-*γ*-*heptylamine*, b.p. 140—142° [*hydrochloride*, m.p. 169—170°; *Ac* derivative (**I**) (prep. by AcCl), m.p. 52—53°]. A partly active (+)-CHEtBu·CO_2H (**II**) gives similarly a (+)-amide, m.p. 100—101°, $[\alpha]^{20}_{4561}$ +0·7° in EtOH, (+)-*γ*-heptylamine, b.p. 140—142°, and thence *d* + *dl*(−)-acet-*γ*-heptylamide (**III**), m.p. 35—45°, b.p. 140—145°/15 mm., $[\alpha]^{21}_{5461}$ −0·6° in EtOH. Beckmann rearrangement of dl-*Me γ-heptyl ketoxime*, b.p. 113—114°/13 mm., leads to (**I**). (**II**), through the (+)-bromide, b.p. 112—113°/24 mm., gives a (+)-Me heptyl ketone, b.p. 71°/13 mm., and thence the oxime, b.p. 116—117°/15 mm., converted (Beckmann etc.) into (**III**), m.p. 30—40°, b.p. 140—145°/17 mm., $[\alpha]^{21}_{5461}$ −0·7° in EtOH. The Curtius and Beckmann reactions are probably true intramol. rearrangements. It is now possible that in the Hofmann, Curtius, Lossen, Beckmann, sulphinate, and (probably) alkylphenol rearrangements, the migrating group ·C*abc* retains its relative configuration during transfer. *dl*-COMeBu-*sec.* gives an o-*carboxyphenylhydrazone*, which could not be satisfactorily resolved through its strychnine salt, m.p. 172—173°.

A. T. P.

Separated auxo-enoid systems. XIV. Preparation of 8-nitro-1-chloromethylnaphthalene and colour of corresponding arylamino-derivatives. V. A. Ismailski and A. N. Kozin (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **28**, 621—624).—1-$C_{10}H_7$·CH_2Cl with HNO_3 (*d* 1·52) and Ac_2O at −2° to 5° gives S-*nitro*-1-*chloromethylnaphthalene* (**I**) (28—42%), m.p. 105°, and substances, m.p. 98—99° and 75°, which may be 5 : 1- (40%) and 4 : 1-NO_2·$C_{10}H_6$·CH_2Cl (14%), respectively. (**I**) is oxidised (15—30% HNO_3) to 8 : 1-NO_2·$C_{10}H_6$·CO_2H (**II**); the impure nitration product similarly gives the 5-NO_2-isomeride in addition to (**II**). The following are prepared from (**I**) (1 mol.) and NH_2Ar (4 mols.) at 60°/1 hr. : 8-nitro-1-anilinomethyl-, m.p. 106°, -1-*p*-, m.p. 74°, and -1-*m*-toluidinomethyl-, m.p. 106°, -1-*p*-, m.p. 150°, and -1-*m*-anisidinomethyl-, m.p. 83·5°, -1-*p*-, m.p. 130°, and -1-*m*-hydroxyanilinomethyl-naphthalene, m.p. 135·5°. The colours of the above derivatives are detailed.

J. L. D.

Alkamine esters of alkylthiol-substituted phenylcarbamic acids. J. J. Donleavy and J. English, jun. (*J. Amer. Chem. Soc.*, 1940, **62**, 2965—2966).—*m*-NO_2·C_6H_4·N_2Cl and OEt·CS_2K in H_2O at 70° give OEt·CS·S·C_6H_4·NO_2-*m*, which by hydrolysis (20% KOH in 70% EtOH) and subsequent treatment with Et_2SO_4 (1 mol.) or $Bu^{\alpha}Br$ (2 mols.) gives m-NO_2·C_6H_4 *Et*, b.p. 117°/3 mm., and *Bu*$^{\alpha}$ *sulphide*, b.p. 135°/3 mm. Sn–HCl then yields m-NH_2·C_6H_4 *Et*, b.p. 103°/3 mm., and *Bu*$^{\alpha}$ *sulphide*, b.p. 131°/3 mm., converted by C_5H_5N (2 mols.) and $ClCO_2Et$ (1 mol.) at the b.p. into m-*ethyl*-, b.p. 165°/4 mm., and m-n-*butyl-thiolphenylurethane*, b.p. 176°/3 mm., which, when distilled with P_2O_5 in vac., give ∼50% of *m*-ethyl-, b.p. 127°/10 mm., and *m*-*n*-butyl-thiolphenylcarbimide, b.p. 129—134°/3 mm. Finally condensation with OH·$[CH_2]_n$·NEt_2 (*n* = 2 or 3) in Et_2O with, later, HCl gives *β*-*diethylaminoethyl* m-*ethyl*-, m.p. 148°, and m-n-*butyl-thiolphenylcarbamate hydrochloride*, m.p. 94°, and *γ*-*diethylamino*-n-*propyl* m-*ethyl*-, m.p. 113°, and m-n-*butyl-thiolphenylcarbamate hydrochloride*, m.p. 158°, which are active but toxic local anæsthetics.

R. S. C.

Dibenzylsulphanilic acid.—See B., 1941, II, 215.

Soluble sulphanilamide derivatives.—See B., 1941, III, 187.

***p*-Hydroxylaminobenzenesulphonamide. Preparation and dimorphism.** H. Burton (*Chem. and Ind.*, 1941, 449).—*p*-NH_2·SO_2·C_6H_4·NH·OH (**I**) has m.p. 139—140° (slow) or 142—143° (rapid heating) (decomp. at 158—160° in both cases) and 160—161° (decomp. 164°) (slow) or 163—164° (decomp.) (rapid heating). The author's method (cf. A., 1941, II, 130) of prep. of (**I**) is superior to that of Bratton *et al.* (cf. A., 1940, III, 436).

H. B.

4-Aminodiphenyl-4′-sulphonamide and [its] derivatives. I. C. T. van Meter, J. A. Bianculli, and A. Lowy (*J. Amer. Chem. Soc.*, 1940, **62**, 3146—3148).—*p*-C_6H_4Ph·NHAc, m.p. 173·6°, and $ClSO_2H$ at <5° give 4-*acetamidodiphenyl*-4′-*sulphonyl chloride* (**I**), decomp. 110°, and thence $[(NH_4)_2CO_3$ and aq. NH_3 at 40° or NH_3–PhMe] the *amide*, m.p. 289° (decomp.), which with boiling 1 : 1 HCl–H_2O gives 4-*aminodiphenyl*-4′-*sulphonamide* (**II**), m.p. 261—262° (slight decomp.) (*Na* salt; hydrochloride). The structure of (**II**) is proved as follows. Boiling 20% HCl hydrolyses (**I**) to *p*-NH_2·C_6H_4·C_6H_4·SO_3H-*p* (also obtained from *p*-C_6H_4Ph·NH_3 by H_2SO_4), the Na salt of which gives a solid diazosulphonate. In H_2O at ∼85° this gives *p*-OH·C_6H_4·C_6H_4·SO_3H-*p*. Fusion with NaOH and 10% of H_2O then gives $(p\text{-OH·}C_6H_4)_2$.

R. S. C.

Preparation of amino-derivatives of diphenylmethane by the reaction of aniline and the toluidines with methylal and formaldehyde. J. F. Salellas (*Rev. Fac. Cienc. Quím., La Plata*, **15**, 307—313).—NH_2Ph with $CH_2(OMe)_2$ and conc. HCl gives a slightly higher yield of $CH_2(C_6H_4$·NH_2-*p*$)_2$ than with CH_2O. The reaction of *m*- also gives a higher yield with $CH_2(OMe)_2$ but that of *o*- and *p*-C_6H_4Me·NH_2 proceeds equally well with either $CH_2(OMe)_2$ or CH_2O.

F. R. G.

Diazotisation. J. Kenner (*Chem. and Ind.*, 1941, 443—447).—A lecture. Conditions for the existence of diazonium and diazo-compounds and their modes of prep. are reviewed. Aliphatic diazonium ions are postulated as the primary unstable products of the action of acids on diazo-paraffins; instability is due to the nucleophilic properties of alkyl groups. When the electrophilic character of the C_6H_6 nucleus is enhanced by, *e.g.*, presence of NO_2, the stability of the ArN_2X is increased. The mechanism of the diazotisation process is discussed.

H. B.

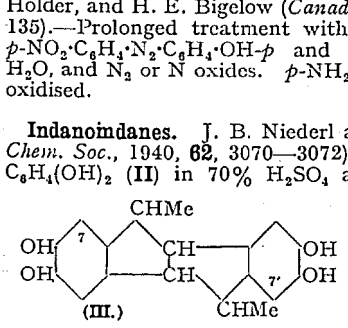
Preparation and properties of diazoaminoazo-compounds. F. P. Dwyer (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 99—106; cf. A., 1941, II, 192).—Benzenediazoaminoazobenzene and MeI–KOH–MeOH afford N-*methylbenzenediazoaminoazobenzene*, m.p. 84—85°. *p*-PhN_2·C_6H_4·N_2Cl added to C_6H_4Me·NH_2 in $COMe_2$–EtOH–NaOAc affords 2-, m.p. 98° (N-*Me* derivative, m.p. 88°), 3-, m.p. 96° (*N*-Me derivative, decomp. on formation to give an aminoazo-compound), and 4-*methylbenzenediazoaminoazobenzene*, m.p. 158° (N-*Me* derivative, m.p. 121°). NO_2·C_6H_4·N_2Cl and *p*-PhN_2·C_6H_4·NH_2–EtOH–NaOAc give 2-, m.p. 171—172° (dimorphous) (N-*Me* derivative, m.p. 132—133°), 3-, m.p. 185—186° (N-*Me* derivative, m.p. 146°), and 4-*nitrobenzenediazoaminoazobenzene*, m.p. 197° (spot reagent for Cd; cf. A., 1937, I, 262) (N-*Me* derivative, m.p. 185—186°). 4 : 1-NO_2·$C_{10}H_6$·N_2Cl affords impure 4-*nitronaphthalenediazoamino-*

azobenzene, m.p. 135° (sensitive spot reagent for Cd) [N-*Me* derivative, m.p. 195° (decomp.)]. *p*-$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}N_2Cl$-*p* and NH_2Ph yield *benzenediazoaminobenzene-4-azo-4'-nitrobenzene*, m.p. 191° (decomp.) (N-*Me* derivative, m.p. 191—192°). The diazoaminoazo-compounds (I) (0·1%) in EtOH (+ trace of alkali) and neutral solutions of metallic nitrates or chlorides, followed by an excess of NaOH, afford colour lakes of undetermined constitution. It is probable that the alkali salt of (I) is adsorbed. Theoretical aspects are considered; it is suggested that H migrates from the triazen to the azo-group to form a *p*-quinonoid structure. Colour lakes prepared from $Mg(OH)_2$ or $Cd(OH)_2$ are described; they are insol. in H_2O or EtOH, and are decomposed by traces of acids. The *N*-Me derivatives do not give colour lakes. A. T. P.

Bromination of phenols by means of bromide–bromate solution. A. W. Francis and A. J. Hill (*Ind. Eng. Chem. [Anal.]*, 1941, **13**, 357).—The overbromination of alkylphenols described by Sprung (A., 1941, II, 94) can be avoided by reduction in the time of bromination, nuclear being very much more rapid than side-chain bromination. A lower KBr/$KBrO_3$ ratio is employed, and bromination is stopped by addition of KI as soon as a yellow colour appears. J. D. R.

Oxidation of 4-nitro-4'-hydroxyazobenzene and related compounds with hydrogen peroxide. E. P. Linton, C. H. Holder, and H. E. Bigelow (*Canad. J. Res.*, 1941, **19, B**, 132—135).—Prolonged treatment with H_2O_2 completely oxidises *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$-*p* and *p*-$OH{\cdot}C_6H_4{\cdot}N_2Ph$ to CO_2, H_2O, and N_2 or N oxides. *p*-$NH_2{\cdot}C_6H_4{\cdot}N_2Ph$ is incompletely oxidised. A. Li.

Indanoindanes. J. B. Niederl and R. H. Nagel (*J. Amer. Chem. Soc.*, 1940, **62**, 3070—3072).—$(CH_2{\cdot}COMe)_2$ (I) with *o*-$C_6H_4(OH)_2$ (II) in 70% H_2SO_4 at room temp. (<1 week) gives 5 : 6 : 5' : 6'-*tetrahydroxy*-1 : 1'-*dimethyldindane* (**III**), m.p. 300° (*tetra-acetate*, m.p. 238—240°, and *-propionate*, m.p. 182°; derived *diquinone*, m.p. 310°).



(III.)

1 : 2 : 3-$C_6H_3(OH)_3$ with (I) in 70% H_2SO_4 first at 100° (short time) and then at room temp. (1 day) gives 5 : 6 : 7 : 5' : 6' : 7'-*hexahydroxy*-1 : 1'-*dimethyldindane*, m.p. 310° (*hexa-acetate*, m.p. 244°). Ac_2 and (II) in 70% H_2SO_4 at room temp. (1 week) give 5 : 6 : 5' : 6'-*tetrahydroxydindane*, m.p. 300° (*tetra-acetate*, m.p. 225°). Absorption spectra of the products are not of anthracene type. R. S. C.

Halogenation of phenolic ethers and anilides. X. Substituted tolyl ethers. B. Jones (*J.C.S.*, 1941, 267—275; cf. A., 1938, II, 484).—Comparative velocity coeffs. for the chlorination in 99% AcOH at 20° of 3 : 1 : 4-$C_6H_3BrMe{\cdot}OR$ [R = Me, Et, CH_2Ph, *p*-$C_6H_4Y{\cdot}CH_2$ (Y = Me, Et, Cl, Br, NO_2), *m*-$C_6H_4F{\cdot}CH_2$, *o*- and *m*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$, and *o*-$C_6H_4Cl{\cdot}CH_2$], 3 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}OR$ (R = Me, Et, Pr^β, Bu^α), 5 : 1 : 2-$C_6H_3BrMe{\cdot}OR$ [R = Me, Et, Pr^α, Pr^β, *n*-C_5H_{11}, CH_2Ph, *p*-$C_6H_4Y{\cdot}CH_2$ (Y = Me, Et, Bu^γ, Cl, Br, NO_2), *m*-$C_6H_4F{\cdot}CH_2$, *o*- and *m*-$C_6H_4Cl{\cdot}CH_2$, and *o*-$NO_2{\cdot}C_6H_4{\cdot}CH_2$], and also 2 : 4 : 1-$C_6H_3Cl_2{\cdot}OR$, 2 : 4 : 1 : 3 : 5-$C_6HCl_2Me_2{\cdot}OR$, and 4 : 2 : 1 : 3 : 5-$NO_2{\cdot}C_6HClMe_2{\cdot}OR$, where R = Me, Et, Pr^α, *n*-C_6H_{13}, CH_2Ph, *o*-, *m*-, and *p*-$C_6H_4Cl{\cdot}CH_2$, *p*-$C_6H_4Br{\cdot}CH_2$, and *m*-$C_6H_4F{\cdot}CH_2$, are recorded. Changes in velocity are to be attributed to variations in the energy of activation, and in ethers of the type *p*-$C_6H_4X{\cdot}OR$ the groups OR and X each contribute a characteristic quota to the activation energy of further substitution. This has been found to be so whenever R = alkyl, benzyl, or substituted benzyl and X a deactivating substituent. When an activating group such as Me is present in the nucleus which undergoes chlorination, the simple additive relationships previously found are not strictly applicable in all cases. With $C_6H_3Cl_2{\cdot}OR$, the same relative directive powers of OR groups are found as for the simpler ethers *p*-$C_6H_4X{\cdot}OR$ (*loc. cit.*); when Me is present in the nucleus undergoing substitution, or when 2 Me are present, *e.g.*, in 2 : 4 : 1 : 3 : 5-$C_6HCl_2Me_2{\cdot}OR$, there is a divergence of ~15% from the mean vals. found for the monosubstituted Ph ethers. When comparison is restricted to $CH_2{\cdot}C_6H_4X$ (X is *m*- or *p*-) ethers, *i.e.*, X is well removed from the point of reaction, the same velocity ratios are observed in the Ph, tolyl, and xylyl series. Comparison of velocity coeffs. of analogous 2 : 4-dichloro- and 2 : 4-dichloro-3 : 5-dimethyl-phenyl ethers shows that the presence of 2 Me increases rate of chlorination >4000 times. The following *ethers* are described: 3 : 1 : 4-$C_6H_3BrMe{\cdot}OR$ (R = p-*methyl*-, m.p. 92°, p-*ethyl*-, m.p. 67°, o-, m.p. 54·5°, and p-*chloro*-, m.p. 67°, p-*bromo*-, m.p. 85°, m-*fluoro*-, m.p. 41°, o-, m.p. 110°, and p-*nitro-benzyl*, m.p. 135°); 3-*nitro*-p-*tolyl* p-*methylbenzyl ether*, m.p. 69°; 5 : 1 : 2-$C_6H_3BrMe{\cdot}OR$ (R = Pr^β, b.p. 129°/19 mm., n-*amyl*-, b.p. 166°/17 mm., and *benzyl*, m.p. 62°; p-*methyl*-, m.p. 83°, p-*ethyl*-, m.p. 81°, p-tert.-*butyl*-, m.p. 99°, o-, m.p. 50°, m-, m.p. 63°, and p-*chloro*-, m.p. 96°, p-*bromo*-, m.p. 117°, m-*fluoro*-, m.p. 73°, o-, m.p. 109°, m-, m.p. 98°, and p-*nitro-benzyl*, m.p. 156°); 2 : 4 : 1 : 3 : 5-$C_6HCl_2Me_2{\cdot}OR$ (R = *Me*, m.p. 82°, *Et*, m.p. 53°, Pr^α, m.p. 31°, *octyl*, m.p. 35°, *benzyl*-, m.p. 89°; p-*methyl*-, m.p. 74°, o-, m.p. 101°, m-, m.p. 88°, and p-*chloro*-, m.p. 99°, p-*bromo*-, m.p. 110°, m-*fluoro*-, m.p. 88°, m-, m.p. 163°, and p-*nitro-benzyl*, m.p. 157°); 2 : 4 : 1-$C_6H_3Cl_2{\cdot}OR$ (R = Me, m.p. 28—29°, Et, m.p. 30—31°, benzyl, m.p. 63°, Pr^α, b.p. 127°/13 mm., Pr^β, b.p. 118°/13 mm.; p-*methyl*-, m.p. 92°, and o-, m.p. 65°, and m-*chloro-benzyl*, m.p. 51°). A. T. P.

Chlorination of diphenyl ether. Orientation [of substituents] in *p*-chlorodiphenyl ether. R. Q. Brewster and G. Stevenson (*J. Amer. Chem. Soc.*, 1940, **62**, 3144—3146).—Chlorination of Ph_2O alone or in CCl_4 is unsatisfactory. In AcOH mainly *p*-$C_6H_4Cl{\cdot}OPh$ (I), b.p. 146—150°/7 mm., with a little (*p*-$C_6H_4Cl)_2O$ (II), m.p. 30°, b.p. 168—172°/7 mm. (lit. an oil), and 3 : 4 : 4'-*trichlorodiphenyl ether* (**III**), m.p. 46—47°, is formed; *o*-$C_6H_4Cl{\cdot}OPh$ (prep. from *o*-$NH_2{\cdot}C_6H_4{\cdot}OPh$), m.p. 47—48°, b.p. 142—146°/12 mm., was not obtained. Further chlorination of (I) (102·5) in AcOH gives 3 : 4-*dichlorodiphenyl ether* (**IV**) (52), b.p. 160—163°/7 mm., (II) (30), and (III) (18 g.). The structure of (III) is proved by its prep. from (II) or (IV), and that of (IV) as follows. 3 : 4 : 1-$NO_2{\cdot}C_6H_3(NH_2){\cdot}OPh$ (prep. from *p*-$NHAc{\cdot}C_6H_4{\cdot}OPh$) gives 4-*chloro*-3-*nitrodiphenyl ether*, b.p. 208—211°/7 mm., reduced by $FeCl_3$–Fe powder in H_2O to 4-*chloro*-3-*aminodiphenyl ether*, b.p. 194—197°/3 mm. (*Bz* derivative, m.p. 92°), which gives (diazo-reaction) (**IV**). Warm Br–AcOH converts (I) into 4-*chloro*-4'- (**V**), m.p. 42—43°, and -3-*bromodiphenyl ether* (**VI**), b.p. 165—168°/7 mm. The structure of (V) follows from its prep. by chlorination of *p*-$C_6H_4Br{\cdot}OPh$ and by diazo-reactions from *p*-$NH_2{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4X$-*p* (X = Cl or Br), that of (VI) from its prep. from *p*-$C_6H_4Cl{\cdot}O{\cdot}C_6H_4{\cdot}N_2Cl$-*m* by CuBr. Chlorination of (V) or bromination of (IV) gives 3 : 4-*dichloro*-4'-*bromodiphenyl ether*, m.p. 52°. 4-*Chloro*-3 : 4'-*dibromodiphenyl ether*, m.p. 49°, is obtained from (VI) or (V) by Br–AcOH. ICl and (I) in boiling AcOH give 4-*chloro*-4'-*iododiphenyl ether* (91%) (**VII**), m.p. 68°. *p*-$C_6H_4I{\cdot}OPh$ and Cl_2–AcOH give *p*-$OPh{\cdot}C_6H_4ICl_2$, m.p. 95—97° (decomp.), converted by hot EtOH into (VII), which is also obtained (diazo-reaction) from *p*-$NH_2{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4Cl$-*p*. By diazo-reactions the appropriate Cl-amine gives 4-*chloro*-3- (**VIII**), b.p. 196—200°/3 mm., -2'-, b.p. 193—196°/3 mm., and -2-*iododiphenyl ether*, m.p. 42°. 1 : 4 : 2-$C_6H_3Cl_2{\cdot}NO_2$ and KOPh give 2 : 4 : 1-$NO_2{\cdot}C_6H_3Cl{\cdot}OPh$. Further iodination of (VII) or (VIII) gives 4-*chloro*-3 : 4'-*di-iododiphenyl ether*, m.p. 73°. HNO_3 (*d* 1·5) in Ac_2O–AcOH at <55° converts (I) into *p*-$C_6H_4Cl{\cdot}O{\cdot}C_6H_4{\cdot}NO_2$-*p*, m.p. 76°, some (II) by disproportionation), and *p*-$C_6H_4Cl{\cdot}O{\cdot}C_6H_4{\cdot}NO_2$-*m* [separated from (II) by reduction]. 4-Chloro-4'-acetamidodiphenyl ether has m.p. 115° (lit. 146°). R. S. C.

Reaction of fluorenone with diazomethane. New route to 9-phenanthrol derivatives. R. F. Schultz, E. D. Schultz, and J. Cochran (*J. Amer. Chem. Soc.*, 1940, **62**, 2902—2904).—CH_2N_2 (prep. *in situ* from NO·NMe·CO_2Et by dry Na_2CO_3) and fluorenone in MeOH–Et_2O give 9-methoxyphenanthrene (30%) (*picrate*, m.p. 157—158·5°), 9-phenanthrol (5%), new m.p. 153—155° (benzoate, new m.p. 99—100°), di-9-phenanthryl ether (1·5%), and a *substance* (1·5%), m.p. 279—281°. R. S. C.

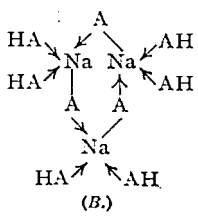
Stable vinyl alcohol, $\alpha\beta$-dimesityl-Δ^α-propen-α-ol. R. C. Fuson, J. Corse, and C. H. McKeever (*J. Amer. Chem. Soc.*, 1940, **62**, 3250—3251).—The stability of sterically hindered enediols is paralleled by that of CRR'·CR·OH, in which R is sterically hindered. Prep. of 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CH_2{\cdot}CN$ from 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CH_2Cl$ by NaCN in aq. EtOH is described. 2 : 4 : 6 : 1-$C_6H_2Me_3{\cdot}CH_2{\cdot}COCl$, *s*-$C_6H_3Me_3$, and $AlCl_3$ in CS_2 give *deoxymesitoin*, m.p. 93·5—94° (oxime, new

m.p. 215—216°), converted by paraformaldehyde and anhyd. Na_2CO_3 in boiling EtOH into *mesityl α-mesitylvinyl ketone*, m.p. 131·5—133°, which with H_2–PtO_2 in EtOH gives *αβ-dimesityl-Δ^α-propen-α-ol*, m.p. 126—127° (*acetate*, m.p. 138—139·5°), unsaturated towards Br and $KMnO_4$. R. S. C.

Enediols. V. Hexa*iso*propylstilbenediols. R. C. Fuson and E. C. Horning (*J. Amer. Chem. Soc.*, 1940, **62**, 2962—2964; cf. A., 1940, II, 343).—2 : 4 : 6 : 1-*Triiso*propylbromobenzene (prep. from *s*-$C_6H_3Pr^β_3$), b.p. 146—148°/18 mm., gives a Grignard reagent and thence 2 : 4 : 6-*tri*iso*propylbenzoic acid*, m.p. 186—187°, the acid *chloride*, m.p. 79—81°, b.p. 107—108°/2 mm., of which with Mg + MgI_2 gives cis-2 : 4 : 6 : 2′ : 4′ : 6′-*hexa*iso*propylstilbenediol* (**I**), m.p. 175—176°. With Ac_2O or Ac_2O–C_5H_5N, (**I**) gives *diacetates*, m.p. (**II**) 214·5—215·5° and 228—230°. Hydrogenation (Pt; MeOH) of 2 : 4 : 6 : 2′ : 4′ : 6′-*hexa*iso*propylbenzil* (**III**) (prep. see below), m.p. 155—156°, gives initially (**I**) and later trans-2 : 4 : 6 : 2′ : 4′ : 6′-*hexa*iso*propylstilbenediol* (**IV**), m.p. 259—260·5° (N_2) [also obtained from (**I**) by H_2–Pt–MeOH; acetylation gives (**II**)]. In air, autoxidation of (**I**) and (**IV**) gives (**III**) only after several hr. and weeks, respectively. (**I**) decolorises Na 2 : 6-dichlorobenzeneone-indophenol immediately; (**IV**) does so more slowly. (**I**) and (**IV**) are insol. in aq. alkali; both are converted into (**III**) by NaOI, (**I**) much more rapidly. Reduction of (**III**) in Ac_2O (Thompson, A., 1939, II, 316) gives a *diacetate*, $C_{36}H_{52}O_4$, m.p. 231—232·5°. 2 : 4 : 6 : 2′ : 4′ : 6′-*Hexa*iso*propylbenzoin*, m.p. 126·5—127·5° (*acetate*, m.p. 114—115·5°), is obtained from (**I**) [not (**IV**)] by HCl–MeOH, but not by spontaneous isomerisation. Ethers of the diols could not be obtained, except by treating (**III**) with MgEtBr in Bu^a_2O–N_2 and then with Me_2SO_4 at the b.p., which yields 2 : 4 : 6 : 2′ : 4′ : 6′-*hexa*iso*propylstilbenediol* Me_2 *ether*, m.p. 178·5—179·5°. During hydrogenation of (**III**), a little AcOH retards and a trace of piperidine favours formation of (**IV**). R. S. C.

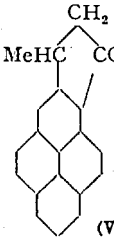
7-Dehydrocholesterol.—See B., 1941, III, 187.

Molecular compounds of phenylacetic acid and its salts. I. A covalent compound of sodium. M. Crawford (*J.C.S.*, 1941, 259—263).—An acid "*salt*" (**I**) of the composition NaA,2HA (A = $CH_2Ph·CO_2$) (probably *B*), m.p. 94·4° (considerably dissociated at m.p.), is prepared by adding Na_2CO_3 (0·5 mol.) to a solution of $CH_2Ph·CO_2H$ (3 mols.) in C_6H_6. (**I**) is sol. in C_6H_6, Et_2O, $CHCl_3$, or H_2O. Mol. wt. determinations of (**I**) in various solvents are made; in PhOH, dissociation into acid and salt is complete at room temp., probably due to formation of (**II**) (below), whilst in ketones there is no association (as in hydrocarbons) suggesting possible combination with the ketone. The binary system HA–NaA is studied. M.p. are determined by recording the point at which growth and not dissolution occurs on seeding. The cooling curve shows the existence of (**I**) and also two distinct eutectic points, corresponding with 11·1% and 47·7% of NaA at 67·5° and 80·5°, respectively. Results differ from those recorded by Bakunin *et al.* (A., 1935, 1323). Evidence is strong for the existence of a compound HA,2NaA and probably one containing 35—40% of NaA. $CH_2Ph·CO_2H$ (1 mol.), PhOH (2 mols.), and Na_2CO_3 (0·5 ml.) give a *compound*, NaA,PhOH (**II**), m.p. 105—125° (sealed tube). $CH_2Ph·CO_2Na$ and COPhMe give the *compound*, NaA,COPhMe, which is decomposed by H_2O and loses COPhMe when crystallised from $COMe_2$. BzOH (3 mols.) and NaOBz (1 mol.) in aq. $COMe_2$ yield the *compound* (**III**), NaOBz,3BzOH, m.p. 227° (sealed tube). Cinnamic acid (2 or 3 mols.) and Na_2CO_3 (0·5 mol.) in aq. $COMe_2$ afford 2 : 1 and 3 : 1 *compounds* (**IV**), not melted <300°, respectively, of acid and Na salt. (**III**) and (**IV**) are insol. in most org. solvents, but dissolve in hot H_2O, AcOH, or PhOH; the acids separate when the hot aq. solutions are cooled. A. T. P.



(*B.*)

Reactions of pyrene. E. Bergmann and E. Bograchov (*J. Amer. Chem. Soc.*, 1940, **62**, 3016—3018).—Pyrene (**I**) and Li in Et_2O give a Li_2 derivative, which with H_2O regenerates (**I**) but with CO_2 gives *pyrene*-4 : 9- or -3 : 10-*dicarboxylic acid*, m.p. 310° (Me_2 ester, m.p. 134°). Pyrene-3-aldehyde, $CH_2(CO_2H)_2$, C_5H_5N, and a little piperidine at 100° and later 150° give β-3-pyrenylacrylic acid (**II**), m.p. 280°, the *Me* ester (**III**) (prep. by MeOH–HCl), m.p. 146°, of which with H_2–Pd(OH)$_2$–$BaSO_4$ in AcOH gives *Me* β-3-*pyrenylpropionate*, m.p. 81°. CH_3N_2–Et_2O converts (**II**) into (**III**) and *Me* β-3-*pyrenylcrotonate* (**IV**), m.p. 105—106°, b.p. 215—217°/0·025 mm. 3-Acetylpyrene, $CH_2Br·CO_2Me$, and Zn in C_6H_6 give a OH-ester, which with 85% HCO_2H at 140° affords (**IV**) and thence by KOH in boiling 15% MeOH β-3-*pyrenylcrotonic acid*, m.p. 233°. $CHMeCl·CH_2·COCl$, (**I**), and $AlCl_3$ in CS_2 at room temp. give (?) 1′-*keto*-3′-*methyl*-3 : 4-*trimethylenepyrene* (**V**), m.p. 101°, b.p. 170°/0·02 mm.; anthracene gives similarly two isomeric ketones, $C_{18}H_{14}O$, m.p. 113° and 82·5°. R. S. C.



(**V.**)

Electrolysis of salts of hexahydrobenzoic acid with nitrates. F. Fichter and A. Petrovitch (*Helv. Chim. Acta*, 1941, **24**, 253—260).—In mixed electrolysis with nitrate, hexahydrobenzoic acid behaves like a fatty acid. In the absence of nitrate the products are di*cyclo*hexyl, *cyclo*hexanol (**I**), *cyclo*hexene, and di*cyclo*hexyl ether obtained from (**I**) by loss of H_2O, *cyclo*hexanone derived from (**I**) by further oxidation, and *cyclo*hexyl hexahydrobenzoate obtained by esterification at the anode. Incorporation of $NaNO_3$ causes the production of cyclo*hexyl nitrate*, b.p. 70—72°/12 mm., and the very unstable dinitrates of *cyclo*hexane-diol and -triol. cyclo*Hexanediol dicarbanilate* has m.p. 207—209°. H. W.

Oxidation of hydroxydiphenyls. J. C. Colbert and C. L. Hensley (*J. Amer. Chem. Soc.*, 1940, **62**, 3257—3258).—Oxidation of Ph_2, hydroxydiphenyls, and homonuclear substituted derivatives thereof by CrO_3–AcOH at the b.p. gives only BzOH (in variable yield). However, the phenolic ring is effectively protected by di-*o*-substitution or by esterification with a heavy group. 3 : 1 : 4-$NO_2·C_6H_3Ph·OH$ gives no BzOH and only a trace of 3 : 1 : 4-$NO_2·C_6H_4(OH)·CO_2H$. 3 : 5 : 1 : 4-$(NO_2)_2C_6H_2Ph·OH$ gives 5% of 3 : 5 : 4 : 1-$(NO_2)_2C_6H_2(OH)·CO_2H$. *o*-$PhSO_3·C_6H_4Ph$ gives 16·35% of *o*-$PhSO_3·C_6H_4·CO_2H$. R. S. C.

Nitration of *p*-nitrobenzoic acid in sulphuric acid solution. Y. P. Liu and T. S. Chin (*J. Chinese Chem. Soc.*, 1940, **7**, 53—61).—*p*-$NO_2·C_6H_4·CO_2H$ (~1 mol.) with 94% HNO_3 (2 mols.) and varying amounts of 5·7% oleum yields 2 : 4 : 1-$(NO_2)_2C_6H_3·CO_2H$ (**I**) in amounts increasing with increasing proportion of oleum, but no 3 : 4 : 1-$(NO_2)_2C_6H_3·CO_2H$ (**II**). Total NO_2-acids are determined by reduction ($TiCl_3$) and titration with Fe^{III} alum and the relative amounts of (**I**) and (**II**) by similar reduction and treatment with excess of KBr–$KBrO_3$ at <0°. A. Li.

[Attempted] preparation of amino-acids by the action of carbon dioxide on the sodium derivatives of cyclic amines. J. F. Salellas (*Rev. Fac. Cienc. Quím., La Plata*, 1940, **15**, 135—142).—Attempts to prepare NH_2-acids by the action of CO_2 on the *N*-Na derivatives of NH_2Ph, NHPhAc, β-$C_{10}H_7·NH_2$, and C_5H_5N were unsuccessful. F. R. G.

Anomalous metalation of triphenylamine. H. Gilman and G. E. Brown (*J. Amer. Chem. Soc.*, 1940, **62**, 3208—3210).—When NPh_3, LiBu^a, and a little Cu-bronze are boiled and then treated with CO_2, m-*diphenylaminobenzoic acid* (**I**) (7%), m.p. 186°, is obtained. NPh_3 does not react with NaPh. *m*-$C_6H_4I·CO_2Me$, $NHPh_2$, K_2CO_3, Cu, and xylene at 190—220° give *Me* m-*diphenylaminobenzoate*, b.p. 205°/3 mm., hydrolysed (KOH) to (**I**). p-*Diphenylaminobenzoic acid*, m.p. 202° (*Me* ester, m.p. 89°), is similarly obtained. PhI, *p*-$NH_2·C_6H_4·CO_2Me$, K_2CO_3, KI, and Cu-bronze in $PhNO_2$ at 200° give *Me* p-*anilinobenzoate*, m.p. 115°, hydrolysed to the *acid*, m.p. 156°. $CPh_2Me·OH$ with LiBu^a (3 mols.) and then CO_2 gives the *lactone*, m.p. 211—212°, of diphenylmethylcarbinol-2 : 2′-dicarboxylic acid. Prep. of the lactone of $OH·CPh(C_6H_4·CO_2H)_2$ from $CPh_3·OH$ (A., 1940, II, 220) is improved by use of 4 mols. of LiBu^a. R. S. C.

Determination of configurations of some hydroxamic acids, oximes, and hydrazones by cryoscopic data. H. C. Yuan and K. C. Hua (*J. Chinese Chem. Soc.*, 1940, **7**, 76—101).—The configurations of stereoisomeric forms of CRR′:N·OH or CRR′:N·NHR″ having an electron-donating atom in a position to form a chelated H-bond can be deduced from cryoscopic data on the assumption that the less associated form has the *syn*-configuration. The prep. and characterisation by mol. wt. determinations in C_6H_6 or $C_{10}H_8$ of the following is de-

scribed: *syn*(OH–OEt)-, m.p. 54°, and *anti*-OEt·CPh:N·OH, m.p. 68°, *syn*(OH–OEt)- (**I**), m.p. 34°, and *anti*-p-C_6H_4Me·C(OEt):N·OH (**II**), m.p. 103°, *syn*(H–OH)-, m.p. 91°, and *anti*-furfuraldoxime, m.p. 75°, *syn*(OH–NPh)-, m.p. 112°, and *anti*-3-anilo-*d*-camphoroxime, m.p. 174°, *syn*-(OH–NH)-, m.p. 36°, and *anti*-*d*-camphorquinone-3-phenylhydrazone, m.p. 188°, *syn*(OH–NH)-, m.p. 102° and 149°, and *anti*-*d*-camphorquinone-3-hydrazone and -acetylhydrazone, m.p. 201° and 234°, respectively. *syn*(NO_2–NH)-, m.p. 75°, and *anti*-NO_2·CH:N·NHPh, m.p. 85°, are characterised from previous data. With PCl_5 in Et_2O, (**I**) yields $CO(NH·C_6H_4Me\text{-}p)_2$, hydrolysed to *p*-$C_6H_4Me·NH_2$, whilst (**II**) yields an oil hydrolysed to *p*-$C_6H_4Me·CO_2H$. A. LI.

Sulphocarboxylic acids. I. Acid chlorides of *m*-sulphobenzoic acid and their reactions with amines and phenols. P. Ruggli and F. Grün (*Helv. Chim. Acta*, 1941, **24**, 197—212).—The prep. of *m*-$CO_2H·C_6H_4·SO_3H$ (**I**), m.p. 133° [NH_2Ph *H* salt, m.p. 224—226°; the $(NH_2Ph)_2$ and Na_2 salts are freely sol. in H_2O], from BzOH and from *m*-$CO_2H·C_6H_4·SO_2Cl$ (**II**) (cf. Smiles *et al.*, *J.C.S.*, 1921, **119**, 1795) is detailed. (**I**) is converted into the diamide, m.p. 175°, and dianilide, m.p. 163°. With β-$C_{10}H_7·OH$ in C_5H_5N–Et_2O at room temp. and then at 70° (**I**) yields *di*-β-*naphthyl* m-*sulphobenzoate*, m.p. 172°. (**II**) and an excess of NH_2Ph in Et_2O give NH_2Ph m-*carboxybenzenesulphonanilide*, m.p. 90°, and the free *acid*, m.p. 212—215° after softening at 180°. (**II**) and β-$C_{10}H_7·OH$ in dil. NaOH afford β-$C_{10}H_7$ m-*carboxybenzenesulphonate*, m.p. 155°; the corresponding Na and Ba salts are respectively sparingly sol. and insol. in H_2O. (**I**) is slowly converted by a large excess of $SOCl_2$ at 40—45° into *m*-$SO_3H·C_6H_4·COCl$ (**III**), m.p. (not pure) 45°, with a halogenated *polyanhydride* (**IV**), m.p. ~140°, which is the main product when boiling $SOCl_2$ is used. The crystallisability of (**III**) depends essentially on the purity of (**I**) employed. (**III**) with an excess of NH_3 in Et_2O gives NH_4 m-*benzamidosulphonate*. With NH_2Ph in Et_2O, (**III**) yields m-*sulphobenzanilide*, m.p. ~120° [NH_2Ph, m.p. 250°, *Ba* (+1H_2O), and *Pb* salts]. β-$C_{10}H_7$ m-*sulphobenzoate* (C_5H_5N, m.p. 74°, *Ba*, and *Na* salts) is obtained from (**III**) or, more conveniently, with isomerisation from (**II**) and β-$C_{10}H_7·OH$ in C_5H_5N at 30° and then at 70°. C_6H_6, (**III**), and $AlCl_3$ give benzophenone-3-sulphonic acid (NH_4 and *Ba* salts; *amide*, m.p. 144°, and its *oxime*, m.p. 155°; *dimethylamide*, m.p. 82—84°), also obtained similarly but in poorer yield from (**IV**). (**II**) gives with C_5H_5N a very unstable *adduct*, m.p. 120—130°. H. W.

Chlorination of diethyl *cis*- and *trans*-hexahydrophthalates. C. C. Price and M. Schwarcz (*J. Amer. Chem. Soc.*, 1940, **62**, 2891—2896).—Hydrogenation (Raney Ni; 175°/100 atm.) of *o*-$C_6H_4(CO_2Et)_2$ gives mixed Et_2 hexahydrophthalates (**I**), hydrolysed to acids (*A*) which are shown by mixed m.p. diagrams to contain 75% of *cis*- and 25% of *trans*-isomeride. AcCl and (*A*) at 100° (bath) give 75% of *cis*-anhydride and thence Et_2 *cis*-hexahydrophthalate (**II**), b.p. 130—132°/9 mm. The *trans*-ester (**III**), b.p. 133—135°/10 mm., obtained from (**I**) by 1% KOH–EtOH, gives the *trans*-acid, new m.p. 219—220°. (**II**) with SO_2Cl_2 and a trace of Bz_2O_2 in boiling CCl_4 gives the α-Cl-ester, which, when distilled, yields Et_2 Δ^1-tetrahydrophthalate, b.p. 142—145°/8 mm. (hydrolysed by 40% KOH and a trace of Na lauryl sulphate to mixed Δ^1- and Δ^2-acids); (**III**) gives similarly, but much faster, the Δ^2-ester, b.p. 148—150°/10 mm. (hydrolysed to the Δ^2-acid, m.p. 214—215°). Since *trans*-elimination of HCl can be assumed, this proves that the intermediate Cl-ester is formed with reversal of configuration (termed bimol. inversion). The H_6-acids and -anhydrides resist chlorination; attempts to prepare the acid chlorides and amides failed. $(CH_2·CO_2Et)_2$ gives a rather small amount of Cl-ester. Hexahydrobenzoyl chloride yields 34% of 1-chlorohexahydrobenzoyl chloride, b.p. 95—96°/18 mm. (derived amide, new m.p. 117—118°, and ethylamide, new m.p. 55—55·5°), and other mixed Cl_1-acid chlorides, b.p. 109—118°/15 mm. (whence a small amount of *amide*, m.p. 210—212°, is obtained). Aromatic compounds give more α-Cl-compounds than do aliphatic compounds; thus, $PrCO_2Et$ gives ≯10, ~50, and 40% of the α-, β-, and γ-Cl_1-derivative, respectively. The above-named reactions are explained by attack by Cl atoms at the rear of the substituted C. This mode of attack can be diagnosed by differences in the mode of reaction of aliphatic and aromatic or *sec.* and *tert.* C derivatives. R. S. C.

Salts of diphenic acid with optically active bases. M. S. Lesslie, E. E. Turner, and E. R. Winton (*J.C.S.*, 1941, 257—259; cf. A., 1934, 538).—The apparent "mutarotation" described previously (*loc. cit.*) for quinine diphenate alcoholate is now shown to be due to an unusually high temp. coeff. Addition curves for diphenic acid (**I**) and nor-*d*-ψ-ephedrine (**II**) show that when (**I**) is in excess over the base in $CHCl_3$, optical activation occurs and results in a preponderance of *d*-base *d*-acid salt; in $COMe_2$ or $COMe_2$–$CHCl_3$ (1 : 4), the *d*-base *l*-acid salt seems to be formed in excess. Rapid mixing of (**I**) and (**III**) in $CHCl_3$ or $COMe_2$–$CHCl_3$ at −30° (cf. A., 1938, II, 490) shows (**I**) to undergo rapid optical activation. The addition curve for (**I**) and cinchonine indicates that the base *d*-acid is much more stable than the base *l*-acid salt in $COMe_2$. When (**II**) is dissolved in $COMe_2$, some mutarotation occurs at room temp.; nor-*d*-ψ-ephedrine diphenate does not similarly show mutarotation. A. T. P.

Further reactions of diphenic anhydride. F. Bell and F. Briggs (*J.C.S.*, 1941, 282—284; cf. A., 1938, II, 495).—Diphenic anhydride (**I**) and $CO(NH_2)_2$ at 120° afford diphenimide and diphenamic acid, but $CS(NH_2)_2$ yields *diphenoylthiocarbamide*, m.p. 231° (decomp.). (**I**) and NH_2Ph or NHPhMe afford N-*phenyl*-, m.p. 181—183°, or N-*phenyl*-N-*methyl*-*diphenamic acid*, m.p. 181°, respectively, hydrolysed by 50% H_2SO_4 to diphenic acid. (**I**) and $NPhMe_2$ with $SnCl_4$ or $AlCl_3$ at 110—120° give green products with properties allied to those of malachite-green; diphenoyl chloride and $NPhMe_2$–$AlCl_3$–CS_2 give a little of a *product*, m.p. 250° (colourless, melts to a green liquid) with the properties of a dye base. (**I**) does not react with 2-methylpyridine, but with 2-methylquinoline (**II**) at 150° affords *quinodiphenone*, m.p. 226—228°. $SnCl_4$, (**I**), and *o*- or *p*-$NH_2·C_6H_4·OH$ or *o*-$OH·C_6H_4·CO_2H$ give fluorenone-4-carboxylic acid, also obtained from (**I**)–$AlCl_3$ at 220°. 2 : 7-Dinitrophenanthraquinone (from the 2-NO_2-compound) is oxidised ($K_2Cr_2O_7$) to 4 : 4'-dinitrodiphenic acid (**III**). 4 : 4'-Dinitrodiphenic anhydride (**IV**) and 15% aq. NH_3 afford 4 : 4'-*dinitrodiphenamic acid*, m.p. 237—239° (decomp.). $AlCl_3$, (**IV**), and *m*-xylene or *s*-$C_6H_3Me_3$ yield 4 : 4'-*dinitro*-2-2'' : 4''-*dimethyl*-, m.p. 207°, or -2-2'' : 4'' : 6''-*trimethyl*-*benzoyldiphenyl*-2'-*carboxylic acid*, m.p. 183—185°, respectively. (**IV**) and (**II**) at 170—190° afford *quino*-4 : 4'-*dinitrodiphenone*, m.p. >300°, and (**IV**) and $CS(NH_2)_2$ at 130—140° give 4 : 4'-*dinitrodiphenoylthiocarbamide*, m.p. 239° (decomp.). (**IV**) and PhEt, PhOH, or *m*-$C_6H_4(OH)_2$ give no cryst. product. (**IV**) undergoes much decomp. with $AlCl_3$ at 220° but some (**III**) is isolable from the reaction mixture. A. T. P.

Steroids and sex hormones. LXVI. Preparation of lactones of the type of digitalis genins. L. Ruzicka, T. Reichstein, and A. Fürst (*Helv. Chim. Acta*, 1941, **24**, 76—82).—Δ^5-3 : 21-Diacetoxypregnen-20-one is converted by Zn and $CH_2Br·CO_2Et$ in C_6H_6 followed by Ac_2O–C_5H_5N at 60° into a mixture separated chromatographically (Al_2O_3) into $\Delta^{5:6\text{-}20:22}$-21-*hydroxy*-3-*acetoxynorcholadienolactone*, m.p. 173—174°, $[\alpha]_D$ −49·5±1·5° in dioxan (whence the Ac-free *compound*, m.p. 260°, $[\alpha]_D$ −46·6°±2° in dioxan), and Δ^5-20 : 21-*dihydroxy*-3-*acetoxynorcholenolactone*, m.p. (indef.) 255—258°, $[\alpha]_D$ −18·9°±2° in dioxan. In C_6H_6 or dioxan the Reformatsky reaction is complicated by partial hydrolysis of OAc at $C_{(3)}$. H. W.

Reaction of copper with benzaldehyde. T. L. Davis and W. P. Green, jun. (*J. Amer. Chem. Soc.*, 1940, **62**, 3014—3015).—Cu and PhCHO with or without PhMe or EtOAc in air (not with peroxide-free PhCHO in vac.), more rapidly if warmed, give the *compound*, $Cu(OBz)_2$,$PhCHO$,H_2O [the anhyd. *complex* is prepared from $Cu(OBz)_2$ and PhCHO at 0°/vac.], from which org. solvents remove the PhCHO. $Cu(OBz)_2$ is reduced by PhCHO at 190°, first to CuOBz and then to Cu. Ag and Hg react similarly, dissolving and later being pptd. as metal. Ni, Mg, Sn, Pb, Zn, and Bi dissolve in PhCHO in air, but the salts formed are not reduced. Pure or impure Fe, Al, Te, Pt, and Au react little or not at all. Cu dissolves also in PrCHO and the resulting Cu butyrate is reduced when heated to Cu. R. S. C.

Acylation of aldoximes. V. Isomerisations in the benzoylation of *syn*- and *anti*-aldoximes in pyridine. (Miss) G. Vermillion and C. R. Hauser (*J. Amer. Chem. Soc.*, 1940, **62**, 2939—2942).—*anti*-CHR:N·OH (R = *p*-anisyl or 3 : 4-CH_2O_2:C_6H_3) and BzCl in C_5H_5N for 24—48 hr. at room temp. or 0° give RCN and little or no *syn*-CHR:N·OBz (*A*) (cf. A., 1940, II, 131), but after 5—10 min. a considerable amount of (*A*) is isolable (cf. Brady *et al.*, A., 1926, 69). In C_5H_5N

saturated with HCl 21—49% of (*A*) is obtained after 5—10 min., but after 36 hr. only a trace of (*A*) and 75% of RCN are formed. When the HCl formed in the reaction (without HCl added) is removed by a strong base (NEt_3 or NPr^{α}_3), only RCN is obtained. Reaction in C_5H_5N thus consists of formation of the *anti*-benzoate (*B*), followed by (*a*) reversible isomerisation by C_5H_5N,HCl to (*A*) and simultaneously (*b*) irreversible conversion of (*B*) by C_5H_5N to RCN + BzOH; after 24 hr. the results of (*a*) are nullified by (*b*). This explanation is supported by conversion of *anti*-3 : 4-CH_2O_2:C_6H_3·CH:N·OH by C_5H_5N,HCl into the *syn*-isomeride within a few min. and by facts in literature. *syn*-CHR:N·OH (R as above or *p*-$NMe_2·C_6H_4$) and BzCl in C_5H_5N give in 17 min. 81—93% of (*A*) and 3% of RCN, but after 9—48 hr. progressively more RCN (reaction mechanism as above); in presence of NEt_3 or NPr^{α}_3 only (*A*) (84—89%) is obtained. R. S. C.

Photochemical bromination of aryl methyl ketones.—See A., 1941, I, 276.

Reduction of α-bromo-ketones by aluminium *iso*propoxide. II. P. G. Stevens and O. C. W. Allenby (*J. Amer. Chem. Soc.*, 1940, **62**, 3264—3265).—COPh·CMe_2Br and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ give (cf. A., 1940, II, 306) a *Pr*$^{\beta}$ *ether*, $C_{13}H_{20}O$, b.p. 84·8—85·0°/9 mm. (with HI gives $Pr^{\beta}I$), alcohols (*A*), b.p. 100·5—103°/9 mm., and a (?) glycol ether, b.p. 113°/9 mm. With CrO_3–AcOH at <23°, (*A*) gives mainly COPhPr^{β} (isolated as 2 : 4-dinitrophenylhydrazone) with some CPhMe_2·CO_2H and probably COMe·CHPhMe (the crude mixture and NaOI give a little CHI_3). This supports the mechanism previously (*loc. cit.*) proposed. R. S. C.

Ethanolysis of Western red cedar, Douglas fir, and Western hemlock. J. S. Brawn, R. D. Heddle, and J. A. F. Gardner (*J. Amer. Chem. Soc.*, 1940, **62**, 3251—3252).—These woods yield by ethanolysis a phenol, which with CH_2N_2 gives α-ethoxypropioveratrone (cf. Hibbert, A., 1939, II, 172). R. S. C.

Michael condensations involving benzyl cyanide. R. W. Helmkamp, L. J. Tanghe, and J. T. Plati (*J. Amer. Chem. Soc.*, 1940, **62**, 3215—3219).—$CO(CH:CHPh)_2$, $CH_2Ph·CN$, and NaOMe–MeOH at room temp. give *δ-keto-αβζ-triphenyl-*Δ^{ϵ}*-heptenonitrile* (*A*), *forms*, m.p. 164° and 144°, and *4-cyano-*3 : 4 : 5-*triphenylcyclohexanone*, m.p. 191° [*oxime*, m.p. 196—198°; 2 : 6-(*CHPh:*)$_2$ derivative, m.p. 196°; obtained also from (*A*) by hot EtOH–NaOH (trace), and, as sole product, by treating the crude reaction products with hot EtOH–NaOH or by carrying out the reaction in boiling MeOH]. $CH_2Ph·CN$, CHPh:$CH·CO_2Et$ (**I**), and NaOEt in cold Et_2O give Et *γ*-cyano-*βγ*-diphenyl-*n*-butyrate (*B*), *forms*, m.p. 59—60·5° and 101·5°. Et 4-cyano-3 : 4 : 5-triphenyl*cyclo*hexanone-2-carboxylate, m.p. 208—209° (Avery, A., 1928, 1243), with boiling HI–AcOH affords the stereoisomeric 4-*cyano*-3 : 4 : 5-*triphenyl*cyclo*hexanone* (**II**), m.p. 213° [*oxime*, m.p. 218—220°; *Me*$_2$ *acetal*, m.p. 192—194°, regenerates (**II**) in boiling conc. HCl–AcOH], which with PhCHO in HCl–EtOH gives the (*CHPh:*)$_2$ derivative, m.p. 237—238°, but in NaOH–EtOH gives *benzylidenebis-*(3-*cyano*-2 : 3 : 4-*triphenyl*-cyclo*hexan*-6-*one*), m.p. 299—301° (decomp.). MgMeI and (**II**) in Et_2O–C_6H_6 give 4-*cyano*-3 : 4 : 5-*triphenyl*-1-*methyl*-cyclo*hexanol*, m.p. 155—158°. $CH_2Bz·CHPh·CHPh·CN$, (**I**), and NaOEt–EtOH at 100° give 4-*cyano*-2-*benzoyl*-3 : 4 : 5-*triphenyl*cyclo*hexanone* (**III**), m.p. 237—237·5° [also obtained from (*B*) and CHPh:CH·COPh by NaOEt–EtOH at 100° or in boiling PhMe], and [from (*B*), m.p. 101·5°] *Et ζ-keto-γ-cyano-βγδζ-tetraphenyl*-n-*heptoate*, m.p. 142—143°. In KOH–MeOH at 0°, (**III**) gives $CH_2Ph·CPh(CN)·CH_2·CO_2H$, and in boiling HI–AcOH gives (**II**). R. S. C.

Constituents of natural phenolic resins. XIX. Action of formalin on 4-keto-6 : 7-dimethoxy-1-3′ : 4′-dimethoxyphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid. R. D. Haworth and G. Sheldrick (*J.C.S.*, 1941, 289—291; cf. A., 1935, 860).—40% aq. CH_2O (2 mols.) with 4-keto-6 : 7-dimethoxy-1-3′ : 4′-dimethoxyphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid (1 mol.) in 8% aq. NaOH at room temp. gives the *lactone* (**I**), m.p. 174° (from MeOH), 120° (from $COMe_2$), and 103—104° (solvated; + $2C_6H_6$), of *4-keto-6 : 7-dimethoxy*-1-3′ : *4′-dimethoxyphenyl*-3 : 3-*bishydroxymethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylic acid*; all three forms yield the same *Ac* derivative, m.p. 160—162°, and (with difficulty) *semicarbazone*, m.p. 242—244° (decomp.). (**I**) and 5% aq. NaOH at 100° (bath) give CH_2O and *4-keto-6 : 7-dimethoxy*-1-3′ : *4′-dimethoxyphenyl*-2-*methylene*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylic acid* (**II**), m.p. 175—177°, which has no ketonic properties and resists lactonisation. The presence of at least one ·CH_2·OH at $C_{(3)}$ is established by reducing (**I**) with Zn–Hg–HCl to an oil, b.p. 240—270°/0·4 mm., converted by Se at 280—300° into 6 : 7-dimethoxy-1-3′ : 4′-dimethoxyphenyl-3-methylnaphthalene. (**II**) affords (Clemmensen) a mixture of the *β*-form, m.p. 209°, of the lactone of 6 : 7-dimethoxy-1-3′ : 4′-dimethoxyphenyl-3-hydroxymethyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid (*loc. cit.*) and 6 : 7-dimethoxy-1-3′ : 4′-dimethoxyphenyl-3-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2-carboxylic acid, m.p. 220—222°. A. T. P.

Pinacol rearrangement of *cis*- and *trans*-7 : 8-diphenylacenaphthene-7 : 8-diols. P. D. Bartlett and R. F. Brown (*J. Amer. Chem. Soc.*, 1940, **62**, 2927—2932).—*cis*-7 : 8-Diphenylacenaphthene-7 : 8-diol (**I**), new m.p. 177·5—178° (corr.), with H_2SO_4 in AcOH–H_2O (more slowly with *p*-$C_6H_4Me·SO_3H$ or without catalyst) at 25° gives 7 : 7-diphenylacenaphthen-8-one, m.p. 175—176° (corr.). The *trans*-isomeride (**II**), new m.p. 158·7—159° (corr.), reacts more slowly. H_2O slows down both reactions. After partial rearrangement of (**II**), much (**I**) is isolated. (**I**) is thus an intermediate in rearrangement of (**II**), the isomerisation being catalysed by H_2O (in the acid medium) or, less well, AcOH. The pinacol rearrangement is catalysed by acid. Reaction mechanisms are discussed. R. S. C.

Hydroxy- and methoxy-phenylanthrones. III. F. F. Blicke and R. J. Warzynski (*J. Amer. Chem. Soc.*, 1940, **62**, 3191—3194; cf. A., 1939, II, 25).—*o*-$CO_2H·C_6H_4·CHPh_2$ and $ZnCl_2$ in Ac_2O at 100° give 10-acetoxy-9-phenylanthracene, oxidised by $Na_2Cr_2O_7$–AcOH–H_2O at 100° to 9-hydroxy-9-phenyl-10-anthrone (**I**), m.p. 211—212° (lit. 208°, 207°). PhOH, (**I**), and a little H_2SO_4 at 100° give 9-phenyl-9-*p*-hydroxyphenyl-10-anthrone, m.p. 253—254° (lit. 251—252°), converted by Me_2SO_4–10% NaOH at 100° into the 9-*p*-anisyl-compound (**II**), m.p. 182—183° (lit. 180—181°), which is also obtained from (**I**) by PhOMe and H_2SO_4 at 100°. *p*-$OMe·C_6H_4·MgI$ and *o*-$CH_2Ph·C_6H_4·COPh$ in boiling Et_2O give *4-methoxy-2′-benzyltriphenylcarbinol*, m.p. 92—93°, cyclised by HCl–AcOH at 100° to 9-*phenyl*-9-p-*anisyl*-9 : 10-*dihydroanthracene*, m.p. 192°, whence (**II**) is obtained (m.p. 183—184°) by $Na_2Cr_2O_7$. AcCl and (**I**) in boiling C_6H_6 give 9-chloro-9-phenyl-10-anthrone, m.p. 165—167° (lit. 164°, 168—169°), which with AgOAc in boiling C_6H_6 gives 9-acetoxy-9-phenyl-10-anthrone, m.p. 196—198° (lit. 194—196°). *o*-$CO_2H·C_6H_4·CHPh·C_6H_4·OH$-*p* (**III**) and $ZnCl_2$–Ac_2O give 10-*acetoxy*-9-p-*acetoxyphenylanthracene*, m.p. 195—196° [also obtained from the *acetate*, m.p. 149—151°, of (**III**)], and oxidised ($Na_2Cr_2O_7$) to 9-*hydroxy*-9-p-*acetoxyphenyl*-10-*anthrone* (**IV**), m.p. 281—282° (decomp.). Hot HCl–AcCl–C_6H_6 converts (**IV**) into 9-*chloro*-, m.p. 187—189°, which with AgOAc–C_6H_6 gives 9-*acetoxy*-9-p-*acetoxyphenyl*-10-*anthrone*, m.p. 205—206°, and with "mol." Ag in C_6H_6 gives a red solution of the radical (amorphous peroxide). Hydrolysis of (**IV**) by boiling NaOH–EtOH–H_2O gives 9-*hydroxy*-9-p-*hydroxyphenyl*-10-*anthrone*, m.p. 208—210° (decomp.), which with Me_2SO_4–NaOH yields 9-hydroxy-9-*p*-anisyl-10-anthrone (**V**), m.p. 205—206°, and with PhOH and a little H_2SO_4 at 100° gives 9 : 9-di-*p*-hydroxyphenyl-10-anthrone, m.p. 305—306° (lit. 308—309°) [Me_2 ether, m.p. 206—207° (lit. 208°)]. *o*-$CO_2H·C_6H_4·CHPh·C_6H_4·OMe$-*p* and $ZnCl_2$ in Ac_2O at 100° give a gummy product, whence $Na_2Cr_2O_7$ yields (**V**) and 9-hydroxy-3-methoxy-9-phenyl-10-anthrone. *o*-$CO_2H·C_6H_4·CH(C_6H_4·OMe$-*p*$)_2$ and $ZnCl_2$–Ac_2O give 2 : 5-di-*p*-anisyl-3 : 4-benzfuran, oxidised to 4-methoxy-2′-anisoylbenzophenone. *o*-$CO_2H·C_6H_4·CH(C_6H_4Cl$-*p*$)_2$ and $ZnCl_2$–Ac_2O give 3-*chloro*-10-*acetoxy*-9-p-*chlorophenylanthracene*, m.p. 155—156°, oxidised to 3-chloro-9-hydroxy-9-*p*-chlorophenyl-10-anthrone. R. S. C.

Reactions of Δ^2-*cyclo*hexenone. Synthesis of di*cyclo*-[2 : 2 : 2]octane-2 : 6-dione. P. D. Bartlett and G. F. Woods (*J. Amer. Chem. Soc.*, 1940, **62**, 2933—2938).—Δ^2-*cyclo*Hexenone (**I**), b.p. 61—63°/14 mm., 169—171° (slight decomp.)/760 mm. [semicarbazone, m.p. 171—172° (decomp.) (lit. 161°); oxime, m.p. 89—90° (lit. 75—76°); 2 : 4-dinitrophenylhydrazone, m.p. 163°], obtained in 35% yield by dehydration (Al_2O_3) of 2-hydroxy*cyclo*hexanone, absorbs 0·99 H_2 (PtO_2; EtOH) to give *cyclo*hexanone, is reduced by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ to Δ^2-*cyclo*hexenol, b.p. 85°/25 mm., and oxidised ($KMnO_4$, $COMe_2$) to $CO_2H·[CH_2]_3·CO_2H$. MgPhBr and (**I**) give phenyl-

*cyclo*hexadiene. $(CH_2{:}CMe)_2$ reacts sluggishly with (I), giving at 185—200° 20% of (? *cis*-)1-keto-6 : 7-dimethyl-Δ^6-octahydronaphthalene, m.p. 62° [*semicarbazone*, m.p. 234° (decomp.)]. $(CH_2{:}CH)_2$ at 180—190° gives (? *cis*-)1-keto-Δ^6-octahydronaphthalene, the *semicarbazone*, m.p. 240° (decomp.), of which yields the (? *trans*-)ketone (oxime, m.p. 153—155°), hydrogenated to *trans*-1-ketodecahydronaphthalene (oxime, m.p. 165·5—166·5°). $CH_2(CO_2Et)_2$ with (I) and a trace of NaOEt at −5° and later room temp. gives Et_2 3-keto-*cyclo*hexylmalonate (90%) (II), b.p. 135—137°/1—2 mm. (*semicarbazone*, m.p. 138—139°). Alkaline hydrolysis of (II) gives the malonic *acid* (III), m.p. 166—168°(decomp.), but the mother-liquor contains material, formed by disproportionation, which by decarboxylation gives (? trans-)3-*hydroxy*cyclo*hexylacetic acid* (IV), m.p. 116—117°. Decarboxylation of (III) gives 3-*keto*cyclo*hexylacetic acid* (V), m.p. 81—82° [Me ester, b.p. 132—133°/9—10 mm. [*semicarbazone*, m.p. 163° (decomp.)], could not be cyclised; also obtained from (IV) by $K_2Cr_2O_7$–H_2SO_4]. (V) yields, best when sublimed over MnO–$CaSO_4$ at 300°/1 mm., *di*cyclo[2 : 2 : 2]*octane*-2 : 6-*dione* (VI) (12%), m.p. 190—191°, the *disemicarbazone*, m.p. 234—236° (decomp.), of which with NaOEt–EtOH gives di-*cyclo*[2 : 2 : 2]octane (57%), m.p. 168—169°. The impossibility of enolisation of (V) (Bredt's rule) reduces reactivity of the α-H. Thus, (V) gives no $FeCl_3$ colour or Cu derivative, is insol. in aq. alkali, and consumes 2 MgMeI, liberating 0·15 mol. of CH_4. R. S. C.

Sterols. CIX. Sapogenins. XXXVIII. Preparation of dihydro*iso*androsterone from diosgenin. R. E. Marker and D. L. Turner (*J. Amer. Chem. Soc.*, 1940, **62**, 3003—3005).—Tigogenone (I) and Ac_2O at 200° followed by hydrolysis (EtOH–KOH) give *ψ-tigogenone*, m.p. 108—111°, which with HCl–EtOH regenerates (I), is oxidised by CrO_3–AcOH at 25—28° to Δ^{16}-*allo*pregnene-3 : 20-dione, and hydrogenated (PtO_2; AcOH; 3 atm.) to tetrahydro-*ψ*-diosgenin (= dihydro-*ψ*-tigogenin) (II). The *diacetate*, m.p. 122—124°, of (II) is converted by CrO_3–AcOH at 30° and later boiling 1% KOH–EtOH into Δ^{16}-*allopregnen*-3(β)-*ol*-20-*one*, m.p. 202—204° (*acetate*, m.p. 162—164°), which with H_2–Pd–$BaSO_4$ in EtOH gives *allo*pregnan-3(β)-ol-20-one (III), and with CrO_3–AcOH gives Δ^{16}-*allo*pregnene-3 : 20-dione. Persulphate oxidation and subsequent hydrolysis of the acetate of (III) gives *dihydro*iso*androsterone*, m.p. 162—164° (*diacetate*, m.p. 124—126°; oxidised to androstanedione), and *allo*pregnane-3 : 21-diol-20-one (*diacetate*, m.p. 151—152°; converted by 5% boiling KOH–EtOH into 3(β)-hydroxyætio*allo*cholanic acid). R. S. C.

Steroids. III. Isolation from equine pregnancy urine of $\Delta^{5:7:9}$-œstratrien-3-ol-17-one. R. D. H. Heard and M. M. Hoffman (*J. Biol. Chem.*, 1941, **138**, 651—665).—A more detailed account of work previously reviewed (A., 1940, III, 903). The hydroxyketone (I) [benzoate, m.p. 196—198° (softens at 190°)] is reduced (H_2, PtO_2, EtOH) to $\Delta^{5:7:9}$-œstratriene-3(β) : 17(α)-diol, m.p. 168—168·5°, identical with one of the products of hydrogenation of equilenin (II). Dehydration ($KHSO_4$ at 150—155° in N_2) of (I) gives $\Delta^{3:5:7:9}$-œstratetraen-17-one, m.p. 114—116°, probably identical with the ketone described by Chakravorty *et al.* (A., 1938, II, 321). It is suggested that (I) is derived from (II) in the body. R. L. E.

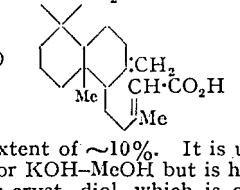
III.—TERPENES.

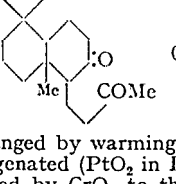
Mol. wt. and constitution of natural caoutchouc. K. H. Meyer and M. Wertheim (*Helv. Chim. Acta*, 1941, **24**, 217—223).—The similarity in the behaviour of natural caoutchouc (I) to linear polymerides in solution and the relationship between η and concn. show (I) to be a straight-chain polymeride with mol. wt. 4—5 × 10^5. Condensations and degradations may result from secondary treatments and cause branched mols. H. W.

Sesquiterpene series. I. Synthesis of the triethyl ester of $C_9H_{15}(CO_2H)_3$ obtained from selinenes. P. C. Dutta (*J. Indian Chem. Soc.*, 1940, **17**, 649—656).—Condensation of 2-methyl-*cyclo*hexanone with OEt·$[CH_2]_2$·I and $NaNH_2$ in Et_2O gives 2-*methyl*-2-β-*ethoxyethyl*cyclo*hexanone* (I), b.p. 100°/6 mm. (*semicarbazone*, m.p. 122°), purified by condensation with $Et_2C_2O_4$ followed by hydrolysis [aq. $Ba(OH)_2$] of the oxalo-derivative. (I) is transformed by HCN at −10° and then at 0° into the *cyanohydrin*, b.p. 147°/9 mm., converted by $SOCl_2$ in C_5H_5N into 2-*cyano*-1-*methyl*-1-β-*ethoxyethyl*-Δ^2-cyclo*hexene* (II), b.p. 118—120°/5 mm. Addition of (II) in C_5H_5N to KOEt–Et_2O gives *Et* 3-*cyano*-4-*methyl*-4-β-*ethoxyethyl*-Δ^2-cyclo*hexenoylformate*, b.p. 168—170°/2 mm. The corresponding acid is converted by oxidation (H_2O_2), reduction (Na–Hg in nearly neutral solution), and esterification into *Me* 3-*cyano*-4-*methyl*-4-β-*ethoxyethyl*cyclo*hexanecarboxylate*, b.p. 145—148°/2 mm., which is transformed by successive treatments with 48% HBr at 140—150°, PBr_5, and EtOH into *Et*$_2$ 2-*methyl*-2-β-*bromoethylhexahydroisophthalate* (III), b.p. 156—160°/3·5 mm., and an unidentified fraction, b.p. 133—138°/3·5 mm. Successive treatments of (III) with KCN in aq. EtOH containing a little NaI and EtOH–H_2SO_4 lead to Et β-1-methyl-2 : 4-dicarbethoxy*cyclo*hexenepropionate, b.p. 170—175°/1 mm. H. W.

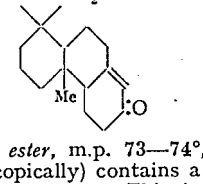
Sesquiterpenes. XLVI. Transformation of guaiol into cadalene. P. A. Plattner and G. Magyar [with, in part, K. Okami] (*Helv. Chim. Acta*, 1941, **24**, 191—197).—The compound $C_{15}H_{26}O_3$, m.p. 220—221°, $[\alpha]_D$ +50°±2° in EtOH, obtained (A., 1931, 1301) by ozonisation of guaiol, is shown by its absorption spectrum and ready loss of H_2O to be a ketone and hence is a dihydroxyketone. The compound $C_{15}H_{22}O$ (I) obtained from it by loss of H_2O under the influence of boiling 0·1N-KOH–EtOH has b.p. 141°/12 mm., $[\alpha]_D$ +127·9°± 1° in EtOH, and is shown spectroscopically to be a doubly unsaturated ketone in which both unsaturated linkings are conjugated with CO. Ozonisation of (I) gives $COMe_2$. (I) is dehydrogenated by Pd–C in a closed tube at 300° to cadalene, identified as the picrate, m.p. 115°, and additive compound, m.p. 112—113°, with 1 : 3 : 5-$C_6H_3(NO_2)_3$. Dehydrogenation in open vessels gives mainly (?) 1-*hydroxy*-2 : 5-*dimethyl*-8-iso*propylnaphthalene*, isolated as the *picrate*, m.p. 132—133°. All m.p. arc corr. It appears that the numerous sesquiterpenes of the type of guaiazulene, like compounds of the vetivazulene, endesmol, and cadalene series, have a regular isoprene chain. H. W.

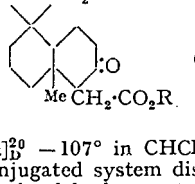
Diterpenes. XLV. Degradation of agathendiacid with ozone. L. Ruzicka, E. Bernold, and A. Tallichet (*Helv. Chim. Acta*, 1941, **24**, 223—237).—Ozonisation proves that the double linkings of agathendiacid (I), m.p. 203—204°, are arranged as in (*A*); it is very possible that isomerides with other arrangements of the double linkings are present in the less homogeneous fractions. The isolation of CH_2O and $H_2C_2O_4$ is most readily effected when the Me_2 ester of (I) is ozonised in CCl_4. The isolation of the neutral compounds is difficult and is best effected after ozonisation in AcOH. A very stable *peroxide*, $C_{18}H_{28}O_5$, m.p. 166—167°, is present to

(*A.*) 

(II.) 

the extent of ~10%. It is unchanged by warming with Zn dust or KOH–MeOH but is hydrogenated (PtO_2 in EtOH) to a non-cryst. diol, which is oxidised by CrO_3 to the *diketo-ester* (II), dimorphous, m.p. 211—213° or 217—219°, $[\alpha]_D^{20}$ +70·7° in CHCl, which is also contained in the neutral products of ozonisation. (II) loses H_2O during distillation, and very readily under the influence of dil. alkali or NaOEt–EtOH and most easily when acted on by NH_2·CO·NH·NH_2,AcOH in MeOH, giving the tricyclic *keto-ester* (III), m.p. 116—117°, $[\alpha]_D^{20}$ +48·7° in $CHCl_3$ (*semicarbazone*, m.p. 231—233°). This is shown spectroscopically to be an αβ-unsaturated ketone. It is converted by MgMeI and subsequent distillation into

(II.I) 

(IV.) 

the *diene ester*, m.p. 73—74°, $[\alpha]_D^{20}$ −107° in $CHCl_3$, which (spectroscopically) contains a conjugated system distributed between two rings. This is partly dehydrogenated (Pd–C at 300—320°) to a *triene ester*, $C_{19}H_{26}O_2$, m.p. 98°, which gives an absorption spectrum with characteristic C_6H_6 bands, and is transformed by Se at 320—330° and then at 350—360° into 1 : 7-dimethylphenanthrene, thus establishing the position

of Me. The acid products of ozonolysis are esterified (CH_2N_2) and treated with Girard's reagent *T*, whereby mainly the *keto-ester* [(**IV**), R = Me], b.p. 165—166°/1 mm., $[\alpha]_D^{20}$ +14·2° in $CHCl_3$, is obtained. It does not give a cryst. oxime or semicarbazone and is partly hydrolysed to the *Me H* ester [(**IV**), R = H], m.p. 173—174°. The Me_2 ester of (**I**) and maleic anhydride at 180° afford a *product*, $C_{28}H_{42}O_8$, b.p. 219—222°/0·1 mm., $[\alpha]_D^{20}$ +28·53° in $CHCl_3$. H. W.

Triterpenes. LVIII. Preparation of *epi*-β-amyrin from α-boswellic acid and from β-amyrone. L. Ruzicka and W. Wirz (*Helv. Chim. Acta*, 1941, **24**, 248—252; cf. A., 1939, II, 435; 1940, II, 137).—Re-examination of the product obtained by treating acetyl-α-boswellaldehyde according to Wolff–Kishner has led to the isolation of *epi*-β-*amyrin*, $C_{30}H_{50}O$, m.p. 225°, $[\alpha]_D$ +73·3° in $CHCl_3$ (*acetate*, m.p. 128°). Hydrogenation of β-amyrone with Na and EtOH in boiling xylene gives almost quant. production of β-amyrin, whereas treatment with H_2 under pressure at 200° in EtOH containing Raney Ni affords unchanged material and the two epimeric β-amyrins. β-Amyrin does not appear to be epimerised by NaOEt–EtOH at 190°. H. W.

Triterpene resinols and related acids. XIII. Bromination of α-amyranonyl benzoate and β-amyranonyl acetate. D. E. Seymour and F. S. Spring (*J.C.S.*, 1941, 319—320).—Bromination (Br–AcOH) of α-amyranonyl benzoate gives *bromo-α-amyranonyl benzoate*, m.p. 177—178° (decomp.), $[\alpha]_D^{20}$ +22·5° in $CHCl_3$, which when heated with AcOH (trace of HBr) affords *iso*-α-amyrenonyl benzoate. β-Amyranonyl acetate similarly yields the *Br*-derivative, m.p. 273—274°, $[\alpha]_D^{27}$ 0° in $CHCl_3$, converted into *iso*-β-amyrenonyl acetate. F. R. S.

V.—HETEROCYCLIC.

Optically active tetrahydrofurfuryl alcohol. M. P. Balfe, M. Irwin, and J. Kenyon (*J.C.S.*, 1941, 312—316).—dl-*Tetrahydrofurfuryl II phthalate*, m.p. 62—64°, is separated through its brucine salts into l-, m.p. 82—82·5°, $[\alpha]_{5893}$ ~ −20° in $CHCl_3$, and d-*forms*, m.p. 82—83·5°, $[\alpha]_{5893}$ +24° in $CHCl_3$, from which, by steam-distillation from 5N-NaOH, may be obtained *d*- and *l*-tetrahydrofurfuryl alcohols. The rotatory dispersion of the alcohol is anomalous. Complex dispersion is also shown by a no. of derivatives. The dl-p-*xenylurethane* has m.p. 104—106°, and the l-p-*nitrobenzoate*, m.p. 36—37°, $[\alpha]_{5893}$ −31·6° in $CHCl_3$. F. R. S.

Formation of methylene ethers by the action of diazomethane on α-keto-lactones and on diphenyl triketone: pyrolysis of coumarandione and allied substances. A. Schönberg, R. Moubasher, and (in part) (Miss) A. Mostafa (*J.C.S.*, 1941, 348—350).—CH_2N_2 and the appropriate dione yield methylene ethers, which when heated with HCl undergo atm. oxidation and are reconverted into the dione: 2 : 3-*methylenedioxycoumarone*, m.p. 110° [from coumarandione (**II**)], *-thionaphthen*, m.p. 130° [from thiocoumarandione (**II**)], -4 : 5-*benzocoumarone*, m.p. 189—190° [from 4 : 5-benzocoumaran-2 : 3-dione (**III**)], and -6 : 7-*benzocoumarone*, m.p. 155° (from 6 : 7-benzocoumaran-2 : 3-dione). $COBz_2$ gives *αβ-methylenedioxy-β-benzoyl-α-phenylethylene*, m.p. 160°, oxidised to the hydrate. Pyrolysis in CO_2 of (**I**) and (**II**) gives respectively xanthone and thioxanthone and of (**III**) some 2 : 3 : 7 : 8-dibenzoxanthone. F. R. S.

Constitution of gmelinol. II. (Miss) R. H. Harradence and F. Lions (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 117—128; cf. A., 1939, II, 170).—Gmelinol (**I**), further purified by chromatographic analysis, is $C_{22}H_{26}O_7$ and not $C_{21}H_{24}O_7$ (*loc. cit.*); it is probably a hydroxypinoresorcinol Me_2 ether. (**I**) is isomerised by a trace of I at 140°, P_2O_5 in xylene, H_2SO_4–AcOH at room temp. for 6 days (best method), $KHSO_4$ at 180°, or HCl–AcOH to *iso*gmelinol, $[\alpha]_D$ +30° in $CHCl_3$. (**I**) could not be catalytically reduced. (**I**) and $KMnO_4$–$COMe_2$ give veratric acid (63% yield assuming two veratrole nuclei). With AcCl (**I**) gives the *acetate*, m.p. 118°, which distils unchanged at 320°/3 mm., and is hydrolysed to (**I**) by KOH–EtOH. (**I**) and $SOCl_2$–C_5H_5N afford *products*, (*a*), m.p. 202° (contains S), and (*b*), $C_{22}H_{26}O_5S_2$, softens at 100°, fuses at 106°, becomes mobile at 150°; neither contains Cl. (**I**) and PCl_3 or PCl_5 give resinous products and (**I**) is decomposed by anhyd. $H_2C_2O_4$ or by vac.-distillation with $KHSO_4$. A. T. P.

2 : 4-Diketo-3 : 3-dialkylpyrrolidines.—See B., 1941, III, 187.

Experiments on the synthesis of the pyridine analogue of vitamin-B_1 (aneurin). (Miss) R. H. Harradence and F. Lions (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 159—168).—Attempts to prepare 2-methyl-2-β-hydroxyethylpyridine are described. OEt·$[CH_2]_2$·CNaAc·CO_2Et and γ-bromopropylphthalimide (**I**) in EtOH afford *Et α-acetyl-α-β'-ethoxyethyl-δ-phthalimidovalerate* (**II**), b.p. 230—235°/5 mm., but attempts to remove the phthalyl residue and the CO_2Et by HCl, NaOH, H_2SO_4, or HBr were unsuccessful: Br·$[CH_2]_3$·NH_2 [from unchanged (**I**)] and possibly δ-amino-α-β'-ethoxyethylvaleric acid or 3-β-ethoxyethyl-2-piperidone were obtained. α-Ethoxypentan-δ-one and 6-aminopiperonal in aq. EtOH–KOH give 2-*methyl*-3-β-*ethoxyethyl*-5 : 6-*methylenedioxyquinoline*, m.p. 83° (*picrate*, m.p. 216°; *methiodide*, m.p. 196°). Attempted hydrolysis by MeOH–KOH (pressure) gave no 5 : 6-$(OH)_2$-compound, and oxidation of the crude hydrolysis product and attempts to obtain a Cu salt of the resulting pyridine-1 : 2-dicarboxylic acid gave only a trace of product. $CHNaAc_2$ and OEt·$[CH_2]_2$·Br–NaI at 180—200° (oil-bath) give β-ethoxyethylacetylacetone, b.p. 114—115°/23·5 mm. (Cu salt, m.p. 183°). The b.p. of Et α-acetyl-γ-ethoxybutyrate is 95—97°/1·5 mm. (cf. Clarke *et al.*, A., 1935, 1510). A. T. P.

Improved syntheses of aminoacridines. I. The five isomeric monoaminoacridines. A. Albert and B. Ritchie (*J.S.C.I.*, 1941, **60**, 120—123).—Amino-5 : 10-dihydroacridines, prepared by reduction of nitroacridones with Na–Hg and EtOH in CO_2 or, more advantageously for larger quantities, Al–Hg in aq. EtOH (suspension made by dissolution in EtOH–NaOH and pptn. with 1 equiv. of HCl), are oxidised directly (cf. Clemo *et al.*, A., 1924, i, 1337) by $FeCl_3$ to aminoacridines in good yield. The mixture of 2- and (mainly) 4-nitroacridone obtained from 3'-nitrodiphenylamine-2-carboxylic acid (**I**) (60% from *o*-C_6H_4Cl·CO_2Na, *m*-NO_2·C_6H_4·NH_2, and catalytic Cu in boiling BuOH) by H_2SO_4 (65% yield) or $POCl_3$ (quant. yield) is reduced (Fe, aq. EtOH–HCl or, better, $SnCl_2$–HCl) to the aminoacridones, which with Na–Hg followed by aq. $FeCl_3$–HCl give 23% and 40%, respectively, of 2- (**II**), m.p. 224° (corr.), and 4-aminoacridine (**III**), m.p. 183° (corr.), separable owing to the relative insolubility of the hydrochloride of (**II**). The mixed aminoacridones obtained from H_2SO_4 and 3'-aminodiphenylamine-2-carboxylic acid [from (**I**), H_2, and Raney Ni] similarly afford (**II**) (70%) and (**III**) (8%); Al cannot be used for reduction since it appears to be inactivated by 4-aminoacridone (? lake formation). 3-Nitroacridone is most conveniently prepared from $POCl_3$ and 4'-nitrodiphenylamine-2-carboxylic acid (55% from *o*-C_6H_4Cl·CO_2Na, *p*-NO_2·C_6H_4·NH_2, and Cu in boiling C_5H_{11}·OH), but 3-aminoacridone (from the NH_2-acid and H_2SO_4) is a more economical starting material for the prep. of 3-aminoacridine (**IV**), m.p. 213—214°. 2-Nitroacridone is obtained (95%) from 5-nitrodiphenylamine-2-carboxylic acid and $POCl_3$. 5-Aminoacridine (**V**), m.p. 241° (corr.), is prepared in 95% yield from 5-chloroacridine, $(NH_4)_2CO_3$, and PhOH at 120°/15 min. 1-Aminoacridine has m.p. 108°. Tannin-mordanted viscose is dyed violet and rose by (**III**) and (**IV**), respectively. (**II**) and (**V**) possess strong antiseptic properties. H. B.

Vitamin-B_6.—See B., 1941, III, 161.

Magnetic studies of co-ordination compounds. II. Effect of distortion of valency bond derivatives of substituted pyrromethenes. D. P. Mellor and W. H. Lockwood (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 141—148; cf. A., 1940, I, 388).—CH_2Ac·CO_2Et–AcOH–aq. $NaNO_2$ at 0—4°, followed by Zn dust and boiling, yield Et 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate, saponifiable to the 3-carbethoxy-5-carboxylic acid, converted by heating (until evolution of CO_2 almost ceases) and distillation at 28 mm. into Et 2 : 4-dimethylpyrrole-3-carboxylate, m.p. 75·3—75·8°. The latter with HCl–HCO_2H at 100° (bath) gives Et 3 : 3' : 5 : 5'-tetramethyldipyrromethene-4 : 4'-dicarboxylate, converted by $Ni(OAc)_2$ or $Pd(NO_3)_2$ in NaOAc–aq. EtOH into the *complexes*, $Ni(C_{38}H_{46}O_8N_4)$ or $Pd(C_{38}H_{46}O_8N_4)$, respectively. Measurements of χ show that the Ni complex is paramagnetic. Large distortion of bond angles may alter considerably the bond character. This is true for the Ni complex when the metal bonds change from covalent to predominantly ionic, but no change in character occurs in the case of Pd. Absorption spectra are given. A. T. P.

Benzoyl derivatives of indigotin. VI. H. de Diesbach and O. Klement (*Helv. Chim. Acta*, 1941, **24**, 158—173).—Et

acetophenone-*o*-carboxylate, obtained from the chloride and EtOH, from the acid, EtOH, and HCl, or from the Ag salt, appears to have the constitution *o*-$C_6H_4Ac{\cdot}CO_2Et$, since it gives a *semicarbazone*, m.p. 181°. The *Me*, b.p. 158°/12 mm., and *Pr*$^{\alpha}$ esters, b.p. 174°/12 mm., are similar. The solid (m.p. 61—62°) Me *ω*-bromoacetophenone-*o*-carboxylate (**II**) is $C_6H_4\langle^{CR(CH_2Br)}_{CO}\rangle O$ (*A*; R = OPh), since it does not yield a semicarbazone, whereas the Et (**II**) and Pr$^{\alpha}$ esters appear to be mixtures of the isomeric forms. *o*-$CH_2Br{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H$ is transformed by $SOCl_2$ into the *chloride*, m.p. 80°, and *anilide*, m.p. 151° (**III**), both of which appear to have the cyclic structure, since they do not exchange Br for NHPh. (**I**) does not react with NH_2Ph at room temp. but when heated with NH_2Ph in C_5H_5N gives appreciable amounts of (**III**), also obtained in ~20% yield from (**II**). An *ester*, m.p. 55°, appears to be *A* with R = OEt. Condensation of isatin with (**II**) by KOH in boiling EtOH–H_2O gives the *lactam*, m.p. 273° (decomp.), of 3-*anilino*-2-*o*-*carboxyphenylquinoline*-4-*carboxylic acid* (**IV**), which passes above its m.p. into the *lactam*, m.p. 276°, of 3-*anilino*-2-*o*-*carboxyphenylquinoline*; the poor yields are due in part to hydrolysis of the ester to acid which loses NH_2Ph in the alkaline liquid, and in part to the production the compound $(CO\langle^{C_6H_4}_{O}\rangle C{:}CH)_2NPh$, m.p. 297°, and derivatives of similar type. (**IV**) is not cyclised by conc. H_2SO_4 but is transformed by P_2O_5 in boiling $PhNO_2$, or by boiling $SOCl_2$ into the *lactam* of 2-*phenyl*-4′-*keto*-1′ : 4′-*dihydroquinolino*-2′ : 3′-3 : 4-*quinoline*-2″-*carboxylic acid*, m.p. 297°; the m.p. and the complete insolubility of this compound in alkaline $Na_2S_2O_4$ show that it is not identical with Ciba-yellow (**V**). $COPh{\cdot}CH_2{\cdot}NPhMe$, isatin, and boiling 40% KOH afford 3-*methylanilino*-2-*phenylquinoline*-4-*carboxylic acid*, m.p. 287°, cyclised by P_2O_5 in boiling $PhNO_2$ to 2-*phenyl*-4′-*keto*-1′-*methyl*-1′ : 4′-*dihydroquinolino*-2′ : 3′-3 : 4′-*quinoline*, m.p. 168°, not identical with the product of the methylation of the hydrate of (**V**). *o*-Cyanoacetophenone, which appears to be a mixture of open and cyclic structures, since it yields a *semicarbazone*, m.p. 216°, but is also sometimes very resistant to hydrolysis, is converted by Br in AcOH or $CHCl_3$ into the *dibromide*, $C_6H_4\langle^{CO}_{CBr(CH_2Br)}\rangle NH$, m.p. 245°. *o*-$C_6H_4AcBr$ reacts readily with Br in AcOH and $CHCl_3$, the first atom appearing to enter the nucleus. At 35° a second mol. of Br reacts, giving an oily, apparently non-homogeneous product which does not react with cold NH_2Ph or hot NH_2Ph–C_5H_5N and gives decomp. products with NH_2Ph in boiling EtOH. The possibility that Br has entered the side-chain is not excluded, since 5 : 2-$NO_2{\cdot}C_6H_3Br{\cdot}CH_2Br$ does not react with cold NH_2Ph and is transformed by NH_2Ph in boiling MeOH into the very unstable 2-*bromo*-5-*nitro*-*ω*-*anilinoacetophenone*, m.p. 114°. *o*-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Br$ does not react with cold NH_2Ph or NH_2Ph–C_5H_5N but is rapidly transformed by NH_2Ph in boiling EtOH into *o*-*nitro*-*ω*-*anilinoacetophenone*, m.p. 157°. *o*-$NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Br$ and NH_2Ph readily afford *o*-*amino*-*ω*-*anilinoacetophenone* (**VI**), m.p. 134°. Attempts to replace NH_2 by Br, I, or CN through the diazonium salt (**VII**) were unsuccessful. When heated with alkali (**VII**) yields a *compound*, $C_{11}H_{11}ON_3$, m.p. 283°. (**VI**) and isatin condense in boiling 33% KOH to 3-*anilino*-2-*o*-*aminophenylquinoline*-4-*carboxylic acid* (**VIII**), m.p. 246°, cyclised by P_2O_5 and $PhNO_2$ at 125—130° to 2-*o*-*aminophenyl*-4′-*keto*-1′ : 4′-*dihydroquinolino*-2′ : 3′-3 : 4-*quinoline*, m.p. 262°, from which NH_2 could not be removed by diazotisation. $NHBz{\cdot}C_6H_4{\cdot}COMe$ is converted by Br in AcOH at 100° into *ω*-*bromo*-, m.p. 122°, transformed by NH_2Ph in boiling EtOH into *ω*-*anilino*-, m.p. 166°, -*o*-*benzamidoacetophenone*, which readily condenses with isatin to (**VIII**). H. W.

Structure of the products of interaction between sodium phenylacetylene and azidochloroethane. S G Fridman and N. N. Lisovskaja (*Ber. Inst. Chem. Akad. Wiss. Ukrain.*, 1940, **6**, 353—365).—$CPh{:}CNa$ and $N_3{\cdot}[CH_2]_2{\cdot}Cl$ in Et_2O give 4-*phenyl*-5-*vinyl*-1 : 2 : 3-*triazole* (15% yield), b.p. 137°/10 mm., oxidised by alkaline $KMnO_4$ to 4-phenyl-1 : 2 : 3-triazole, m.p. 146—147°, and with Br giving 4-*phenyl*-5-*αβ*-*dibromoethyl*-1 : 2 : 3-*triazole*, m.p. 156—157°. J. J. B.

Action of organo-alkali compounds on benzonitrile. R. M. Anker and A. H. Cook (*J.C.S.*, 1941, 323—331).—The reaction between PhCN and a no. of alkali alkyls, aryls, and aralkyls in Et_2O and other inert solvents at room temp. gives either triphenylalkyldihydrotriazines or polyphenylpyrazolines. Products of the first type which contain a primary alkyl group liberate NH_3 on heating to comparatively low temp., forming 2 : 4 : 6-triphenylpyrimidines, so that the parent compounds are 1 : 3 : 5-triazines. The mechanism of these reactions is discussed and reasons are advanced for the formation either of pyrazolines or of dihydrotriazines. MeLi and PhCN give 2 : 4 : 6-*triphenyl*-2-*methyl*-1 : 2-*dihydro*-1 : 3 : 5-*triazine*, m.p. 62°, remelts 143° [*sulphate*, m.p. 264°; *hydrochloride*, m.p. 248° (decomp.); p-$C_6H_4Me{\cdot}SO_2$ derivative, m.p. 240—241°; N-*NO*-compound, m.p. 205° (decomp.)], which when heated forms 2 : 4 : 6-triphenylpyrimidine, also obtained from 6-*chloro*-2 : 4-*diphenylpyrimidine*, m.p. 108°, and MgPhBr. The lithiodihydrotriazine and MeI yield 2 : 4 : 6-*triphenyl*-1 : 2-*dimethyl*-1 : 2-*dihydro*-1 : 3 : 5-*triazine*, m.p. 156°. EtLi with PhCN similarly gives 2 : 4 : 6-*triphenyl*-2-*ethyl*-1 : 2-*dihydro*-1 : 3 : 5-*triazine*, m.p. 155°, forming when heated 2 : 4 : 6-*triphenyl*-5-*methylpyrimidine*, m.p. 182°, also prepared from MgPhBr and 6-*chloro*-2 : 4-*diphenyl*-5-*methylpyrimidine*, m.p. 118°, obtained from the 6-*OH*-compound, m.p. 253° (from $CHBzMe{\cdot}CO_2Et$ and $NH_2{\cdot}CPh{:}NH,HCl$). The similar series of substances from Pr$^{\alpha}$Li are 2 : 4 : 6-*triphenyl*-2-*n*-*propyl*-1 : 2-*dihydro*-1 : 3 : 5-*triazine*, m.p. 50°, remelts 116° (*sulphate*, m.p. 222°), 2 : 4 : 6-*triphenyl*-5-*ethylpyrimidine*, m.p. 127°, and 6-*hydroxy*-, m.p. 266°, and 6-*chloro*-2 : 4-*diphenyl*-5-*ethylpyrimidine*, m.p. 122°. 2 : 4 : 6-*Triphenyl*-2-*isopropyl*-1 : 2-*dihydro*-1 : 3 : 5-*triazine*, m.p. 184°, does not evolve NH_3 when heated. The compounds obtained from Bu$^{\alpha}$Li are 2 : 4 : 6-*triphenyl*-2-*n*-*butyl*-1 : 2-*dihydro*-1 : 3 : 5-*triazine*, m.p. 40—50°, remelts 117° (*alcoholate*; *sulphate*, m.p. 215°; *hydrochloride*, m.p. 256°); 6-*hydroxy*-, m.p. 235°, and 6-*chloro*-2 : 4-*diphenyl*-5-*n*-*propylpyrimidine*, m.p. 133°; and 2 : 4 : 6-*triphenyl*-5-*n*-*propylpyrimidine*, m.p. 135°. $NaCHPh_2$ and PhCN give 3 : 4 : 4 : 5-*tetraphenylpyrazoline*, m.p. 213°, oxidised (CrO_3–AcOH) to 3 : 4 : 4 : 5-*tetraphenylpyrazole*, m.p. 175°, and converted by Ac_2O into $CHPh_2{\cdot}COPh$. CPh_2N_2 and stilbene afford 3 : 3 : 4 : 5-*tetraphenylpyrazoline*, m.p. 163°. F. R. S.

Synthesis of theophylline. F. L. Grinberg (*J. Appl. Chem. Russ.*, 1940, **13**, 1461—1463).—Traube's synthesis (A, 1901, i, 54) is repeated. 5 : 6-Diamino-2 : 6-diketo-1 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydropyrimidine is formylated by boiling 48% HCO_2H in 90 min. R. T.

Porphyrins. II. Crystallisation of methyl esters of porphyrins. M Grinstein (*Anal. Asoc. Quim. Argentina*, 1941, **29**, 5—14).—Esterification of copro- or uro-porphyrin (**I**) with MeOH–C_6H_6 permits almost complete pptn. of the ester and its rapid drying. Esterification of (**I**) with MeOH–dioxan gives a slow-drying product. Crystallisation from C_6H_6–ligroin is preferred. F. R. G.

Ultra-violet absorption spectra of metallo-porphyrins and their compounds with globin.—See A., 1941, I, 292.

Alkaloids of Bulgarian belladonna root. H. King and L. L. Ware (*J.C.S.*, 1941, 331—337).—The alkaloids have been separated by King's method (*J.C.S.*, 1920, **117**, 991) and *l*-hyoscyamine, *l*-hyoscine, tropine, and bellaradine (**I**), $C_7H_{13}ON$, have been isolated. The N of (**I**) is *tert.* and a pyrrole nucleus is present; (**I**) forms a *methiodide*, m.p. 253°, *methopicrate*, m.p. 228°, and a *picrate*, m.p. 224—225° (decomp.), which is not identical with *nor*-*ψ*-*tropine picrate*, m.p. 187—188°. The quantity of (**I**) is so small that it is unlikely that the efficacy claimed for the root depends on its presence. F. R. S.

2-Acetyl-1-methylpyrrolidine. H. King (*J.C.S.*, 1941, 337—339).—Proline is converted (MeI–MeOH) into stachydrine, which on dry distillation gives Me hygrate. This condenses with EtOAc ($NaNH_2$–C_6H_6) to Et 1-methylpyrrolidoyl-2-acetate, which, heated with HCl–H_2O, gives CO_2 and 2-acetyl-1-methylpyrrolidine (*aurichloride*, m.p. 108—109°), not identical with bellaradine nor with the product of Hess *et al.* (A., 1916, i, 67). F. R. S.

New synthesis of nornicotyrine and of its oxygen analogue. F. Lions and E. Ritchie (*J. Proc. Roy. Soc. N.S. Wales*, 1940, **74**, 110—116).—Et nicotinylacetate hydrochloride, aq. NH_3, and $CH_2Cl{\cdot}CHCl{\cdot}OEt$ at −10° to −15°, then at room temp., afford *Et* 2-(3′-*pyridyl*)*pyrrole*-3-*carboxylate* (**I**), m.p. 118°, and (mainly) *Et* 2-(3′-*pyridyl*)*furan*-3-*carboxylate* (**II**), b.p. 148—150°/1·5 mm. (*picrate*, m.p. 153°). The *acid* from (**I**), m.p. 212—214° (evolves CO_2), with Cu powder at 230°/2 mm. gives nornicotyrine, m.p. 98—99° [picrate, m.p. 203—204°

(decomp.)]. Similarly (II) affords 2-(3′-*pyridyl*)*furan*-3-*carboxylic acid*, m.p. 225°, and 2-(3′-*pyridyl*)*furan*, b.p. 127—128°/25 mm. [*picrate*, m.p. 152°; *methiodide*, m.p. 221—222° (decomp.)]. A. T. P.

Cadmium iodide complex of narcotine. P. Duquénois and M. Ellert (*Rev. Fac. Sci. Istanbul*, 1940, **5**, 99—101).—Narcotine hydrochloride with an excess of CdI_2 or Marmé's reagent in feebly acid solution gives a *substance*, $(C_{22}H_{23}O_7N,HI)_2,CdI_2$, m.p. 140° (decomp.) after sintering ~125°. J. L. D.

VII.—PROTEINS.

Thiol groups of ovalbumin. M. L. Anson (*J. Gen. Physiol.*, 1941, **24**, 399—421; cf. A., 1940, III, 930).—The reaction of SH groups of denatured ovalbumin (I) [in aq. guanidine hydrochloride (II) or long-chain alkyl sulphate] with $Fe(CN)_6'''$ or *p*-chloromercuribenzoate (III) is more rapid than that with S_4O_6''; the oxidation by $Fe(CN)_6'''$ is inhibited by CN′. Impure (II) (purification described) contains impurities that cause abolition of the SH groups of denatured (I). The SH groups can also be abolished by treatment of the native (I) with I, a process in which few of the SH groups go beyond ·S·S· or the tyrosine groups go into di-iodotyrosine groups. The compound of (III) and SH groups does not give a nitroprusside test or reduce $Fe(CN)_6'''$ but reduces I. The rôle of SH groups in protein structure is discussed. F. O. H.

VIII.—ANALYSIS.

Semi-micro-determination of sulphur in organic compounds. R. M. Lincoln, A. S. Carney, and E. C. Wagner (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 358—361).—A Parr bomb suitable for semi-micro-determination of S in samples of ~50 mg. by Na_2O_2 fusion is described in detail. The substance is mixed with $KClO_4$, Na_2O_2, and sucrose, and after combustion the acidified solution is pptd. with $BaCl_2$ in presence of picric acid (I), and the S determined as $BaSO_4$. The use of (I) renders the $BaSO_4$ filterable in a shorter time. A procedure is outlined for the removal of H_2SiO_3, introduced when liquid samples in glass ampoules are decomposed in the bomb. An accuracy of ±0·3% is usually obtained. J. D. R.

Analytical procedure for mixtures of organic sulphur compounds. R. T. Bell and M. S. Agruss (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 297—299).—The material is diluted with C_6H_6 and a sample shaken with aq. $CdCl_2$ to remove H_2S. Mercaptans and H_2S in the original solution, and mercaptans in the H_2S-free solution, are determined by $AgNO_3$–NH_4CNS. If mercaptan-S is >1%, mercaptans are removed by 10% $AgNO_3$ and the solution is washed successively with EtOH–morpholine and H_2O, and disulphides are determined in the solution by reduction with Zn–AcOH followed by determination as mercaptans. CS_2 is determined by conversion into xanthic acid with KOH–EtOH, which is titrated with 0·1N-I, and sulphides by oxidation with Br–H_2O followed by determination of HBr liberated. J. D. R.

Lanthanum nitrate test for acetate in inorganic qualitative analysis. K. Neelakantam and L. R. Row (*Proc. Indian Acad. Sci.*, 1941, **13**, A, 194—197).—Modifications in the $La(NO_3)_3$ test for OAc′ ions are discussed. SO_2 interferes. W. R. A.

Methoxyl determination. Modification of apparatus and preparation of hydriodic acid. B. E. Christiansen, L. Friedman, and Y. Sato (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 276—277).—A modified apparatus for the Vieböck determination of OMe is described. The importance of the purity of the HI is stressed, the presence of org. halides or org. matter being a common source of error. It is recommended that the HI be freshly prepared by distillation of KI with 80% HPO_3 in an all-glass apparatus. J. D. R.

Micro-analysis of gaseous hydrocarbons. L. Marion and A. E. Ledingham (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 269—271).—A detailed description is given of the construction and manipulation of a gas burette by which small quantities (3—5 mg.) of gaseous hydrocarbons are introduced into the normal Pregl combustion train. The combustion is carried out in the usual way, and from the vol. of gas used and the sum of the wts. of C and H produced the mol. wt. is also determined. J. D. R.

Methods of analysis for acetylene, acetic acid, acetic anhydride, acetone, ethyl acetate, and mercury. G. S. Shaw (*Canad. Chem.*, 1941, **15**, 197—200).—C_2H_2 is absorbed in $Cu_2Cl_2,2NH_4Cl$; H_2S is determined as CdS (from $CdCl_2$), and org. S and PH_3 are determined by burning the C_2H_2 and absorbing the SO_2 or P_2O_5 respectively in S-free H_2O containing Na_2O_2, and weighing as $BaSO_4$ or $Mg_2P_2O_7$, respectively. AcOH is determined by titration (NaOH) or f.p. method; any MeCHO is determined by $NaHSO_3$, HCO_2H by NaOBr–KI–HCl (titrate with $Na_2S_2O_3$), H_2SO_4 by a tintometer method, chlorides by $AgNO_3$, and sulphates by $BaCl_2$; tests for Fe and heavy metals are given. Ac_2O is determined by total acidity, or by the NH_2Ph or hydration method. Tests for colour, *d*, H_2O content and acidity or alkalinity of $COMe_2$, and also for acidity, dryness, saponification, b.p. range, and MeCHO content, of EtOAc, are recorded. Hg is determined by dissolving in 50% HNO_3 with a little $KMnO_4$–H_2O_2, and titrating with KCNS (halogens interfere) [$HgNO_3 + 2KCNS = Hg(CNS)_2 + 2KNO_3$]. A. T. P.

Determination of the proportion of *d*- and *l*-isomerides in samples of lactic acid. S. Moore, R. J. Dimler, and K. P. Link (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 160—163).—The lactic acid (I) is heated at 135° for 2 hr. with *o*-$C_6H_4(NH_2)_2$, HPO_3, and EtOH, and the resulting 2-α-hydroxyethylbenziminazole is pptd. as the Ag salt (II) with $AgNO_3$–NH_3. The dried, weighed (II) is decomposed with HCl and the α of the solution is determined. The % of *d*- and *l*-isomerides in the original (I) is calc. from the wt. of (II) taken and the α of the solution. The use of the benziminazole derivative of (I) offers the following advantages over the Zn salt formerly used: a fourfold increase in α ($[\alpha]_D$ −32·7°), negligible variation of α with concn., and absence of fractionation of isomerides during pptn. and isolation of the derivative. J. D. R.

Micro- and drop-scale titrations of oxalate. P. L. Kirk and P. C. Tompkins (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 277—280).—The micro- and drop-scale titrations of oxalate and of Ca determinations using $Ce(SO_4)_2$, NH_4 hexanitrato- and hexaperchlorato-cerate (I), and $KMnO_4$ as reagents are compared. The excess $Ce(SO_4)_2$ method has the widest applicability for both scales, and is capable of the greatest accuracy. $KMnO_4$ can be used for micro- and drop-scale work, using *o*-phenanthroline–$FeSO_4$ as indicator, but (I) is unsatisfactory on the drop scale unless the indicator is added near the end-point. Micro-titrations with $KMnO_4$ are improved by titrating the cold solution, using setopaline *C* indicator internally and using $MnSO_4$ as catalyst. Errors in both scale titrations are only ~1%. J. D. R.

Determination of formaldehyde with 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione. J. H. Yoe and L. C. Reid (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 238—240).—Very accurate results can be obtained in the determination of CH_2O with dimethyl*cyclo*hexanedione (I) if the pptn. is carried out at p_H 4·6 (NaOAc–HCl buffer). At this p_H, only 0·166 mg. of CH_2O per l. remains unpptd., and 1·3 mg. each of MeCHO and EtCHO from similar solutions. The ppt. should be given 12 hr. to form and, after filtration, dried at 60° for several hr. The efficiency of pptn. of CH_2O, MeCHO, and EtCHO with (I) is greatly dependent on p_H, and 4·6 is the optimum val. in all three cases. J. D. R.

Rapid determination of reducing sugars. Extension of Forsee's photocolorimetric ferricyanide method. S. A. Morell (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 249—251).—The range of Forsee's method (A., 1938, III, 860) has been extended to the photocolorimetric determination of samples containing up to 1·2 mg. of reducing sugar. The decrease in yellow colour caused by the reduction $K_3Fe(CN)_6 \rightarrow K_4Fe(CN)_6$ is measured with an Evelyn photo-electric colorimeter, and minor variations in technique permit numerous analyses in a short time. J. D. R.

Reducing properties of *l*-sorbose. F. K. Broome and W. M. Sandstrom (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 234—235).—The reducing properties of *l*-sorbose (I) and of fructose (II) are determined, using $K_3Fe(CN)_6$ (III) and $Ce(SO_4)_2$. Direct titration is satisfactory for (I) in concn. 0·01—0·70%; below this range accuracy is reduced and above it (III) is completely reduced. The similarity of the reducing powers of (I) and (II) supports the hypothesis that reducing power is due to the configuration of OH groups at $C_{(3)}$ and $C_{(4)}$. J. D. R.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

SEPTEMBER, 1941.

I.—ALIPHATIC.

Reaction of free methyl radicals with nitric oxide.—See A., 1941, I, 339.

Isomerisation of pentanes.—See A., 1941, I, 336.

Mechanism of reaction and of poisoning in the dehydroaromatisation of *n*-heptane. H. S. Taylor and H. Fehrer (*J. Amer. Chem. Soc.*, 1941, **63**, 1387—1392; cf. A., 1941, I, 341).—The rate of dehydrogenation of *n*-C_7H_{14} over 10 : 1 Cr_2O_3–SnO_2 at 475° is initially >, but soon becomes <, that of *n*-C_7H_{16}. At 450° 15% of *n*-C_7H_{14} added to *n*-C_7H_{16} depresses the rate of dehydrogenation of the latter and slightly increases the amount of aromatisation. In presence of Cr_2O_3 gel at 475° methyl*cyclo*hexane is dehydrogenated faster than is *n*-C_7H_{14} or -C_7H_{16} and does not poison the catalyst. The poisoning due to *n*-C_7H_{14} is accompanied by deposition on the catalyst of a substance removed by O_2 but not by N_2 or H_2; prior treatment of Cr_2O_3 gel with *n*-C_7H_{14} greatly reduces its efficiency. Dehydrogenation of mixtures of C_7H_{14} and C_7H_{16} gives more olefine and less aromatisation as the reaction (and poisoning) proceeds. Thus the main effect of the poisoning is on aromatisation. Various Cr_2O_3 and, to a smaller extent, Mo, Mn, Ce, and V catalysts behave similarly. Increase in temp. increases the amount of aromatisation. The kinetics are discussed. R. S. C.

Two-component gel catalysts containing chromium oxide for aromatisation of *n*-heptane.—See A., 1941, I, 341.

Use of sulphuric acid in purifying saturated hydrocarbons. Its action on ββδ-trimethylpentane. F. C. Whitmore and H. H. Johnson, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 1481—1482).—$CH_2Pr^{\beta}Bu^{\gamma}$ and 95% H_2SO_4 at ~20° in 3 days give SO_2, <25% of $CH_2Pr^{\beta}Bu^{\gamma}$, and 39% of material of b.p. <96°/740 mm., and 31% of b.p. >123°/740 mm. Bu^{γ}_2 and $CH_2Bu^{\gamma}_2$ are probably formed. The possibility of rearrangement during treatment of paraffins with H_2SO_4 must thus be considered. R. S. C.

Formation of propylene by dehydrogenation of propane.—See B., 1941, II, 209.

Preparation of butadiene from αγ-butylene glycol by dehydration in the vapour phase. I, II.—See B., 1941, II, 209.

Kinetics of olefine–bromine reaction. Influence of catalysts.—See A., 1941, I, 340.

Polymerisation of olefines. IV. Nonenes formed by dehydration and co-polymerisation of *tert.*-butyl and -amyl alcohols. F. C. Whitmore and L. W. Nixon (*J. Amer. Chem. Soc.*, 1941, **63**, 1460—1462; cf. A., 1941, II, 181).—1 : 1 $Bu^{\gamma}OH$–$CMe_2Et{\cdot}OH$ with 65% H_2SO_4 at 80° gives $CH_2{:}CMe_2$ (0·5), *iso*-C_5H_{10} (30), di*iso*butylenes (22), nonenes (17), diamylenes (6), tri*iso*butylenes (6), and higher polymerides (1·5%). The nonenes are shown by ozonisation of fractions to consist of $CHMeBu^{\gamma}{\cdot}CMe{:}CH_2$ (50), $CHMe{:}CMe{\cdot}CH_2Bu^{\gamma}$ (23), $CMeBu^{\gamma}{:}CMe_2$(10), $CMe_2{:}CH{\cdot}CMe_2Et$ (10), and $CMeEt{:}CHBu^{\gamma}$ (5%), absence of the trimethyl-Δ^{α}-hexene being remarkable. R. S. C.

Detection of diacetylene in presence of acetylene. I. I. Strishevski and M. D. Tschechovitsch (*J. Gen. Chem. Russ.*, 1940, **10**, 1303—1304).—2 ml. of a 1% solution of $CuSO_4,5H_2O$ in 5% aq. NH_3 are added to 2 ml. of solution; a ppt. is given immediately by $(CH{:}C)_2$. The $(CH{:}C)_2$ content of the solution is derived from the Cu content of the ppt. R. T.

Atmospheric oxidation of Δ⁵-dodecinene. M. J. Murray and F. F. Cleveland (*J. Amer. Chem. Soc.*, 1941, **63**, 1363—1364).—When kept in air in diffuse light, $(n\text{-}C_5H_{11}{\cdot}C{:})_2$ yields a fraction, b.p. 89—90°/1—2 mm. [impure 2 : 4-*dinitrophenylhydrazone* (I), m.p. 59°], shown by Raman spectra and synthesis to be mainly Δ⁵-*dodecinen*-ε-*one* (II). *n*-$C_5H_{11}{\cdot}C{:}C{\cdot}MgCl$ and $(Bu^{\alpha}CO)_2O$ give (II) and thence (I), m.p. 65°. Other disubstituted acetylenes are similarly oxidised. R. S. C.

Synthesis of alkyl halides.—See B., 1941, II, 211.

Removal of substituents from vinyl polymerides. R. Simha (*J. Amer. Chem. Soc.*, 1941, **63**, 1479—1481).—Removal of substituents from polymerides is considered statistically. R. S. C.

Production of alcohols from olefines.—See B., 1941, II, 212.

Derivatives of allylic chlorides. Reactions of methallyl alcohol. G. Hearne, M. Tamele, and W. Converse (*Ind. Eng. Chem.*, 1941, **33**, 805—809; cf. A., 1941, II, 158).—β-Methylallyl alcohol (I) or di-β-methylallyl ether (cf. Tamele *et al.*, A., 1941, II, 82) when distilled from 12% H_2SO_4 (still-head temp. 61°) gives $Pr^{\beta}CHO$ (II), b.p. 64·1° (azeotrope with 5% of H_2O, b.p. 60·5°), nearly quantitatively, the latter being readily oxidised to $Pr^{\beta}CO_2H$. If the temp. of distillation rises above 61°, *iso*butylene glycol *iso*butyracetal (III), b.p. 138—139° (cf. Dolgorukova-Dobryanska, A., 1926, 818) is formed. When $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$ (IV) or (I) is boiled with 12% H_2SO_4 for 1 hr., (III) is formed, but distillation of the mixture gives (II) nearly quantitatively. (III) with boiling 12% H_2SO_4 gives (II) slowly but rapidly if (II) is distilled off. When (I) and (II) are boiled in acid solution, (III) and a little (IV) are formed, indicating that one reaction is (I) → (IV) → (II) and that (III) is formed by interaction of (II) and (IV). (I) is converted into (II) by heating it with H_2SO_4 in $Pr^{\beta}CO_2H$ or by passing the vapour over pumice or activated charcoal at 200—400°. Distillation of $CHMe{:}CMe{\cdot}CH_2{\cdot}OH$ with 13% H_2SO_4 gives $COMePr^{\beta}$ (V) (72%) and $CHMeEt{\cdot}CHO$ (VI) (28%). Similarly, $CH_2{:}CMe{\cdot}CHMe{\cdot}OH$ gives (V) (88%) and (VI) (12%). When (I) is heated with the appropriate org. acid, an ester is formed, and with H_2 (pressure)–Ni below 200° gives $Bu^{\beta}OH$. Dehydrogenation of (I) at 500° gives $CH_2{:}CMe{\cdot}CHO$ (VII) inseparably mixed with (II). (I) with air–Ag gauze at 500° gives (VII) as a continuous process. At higher temp., CO, olefines, and some CO_2 are also formed. Oxidation in pure O_2 leads to some dehydrogenation and a little (II) is formed. (VII) rapidly polymerises in air, the reaction being facilitated by light, moisture, and heat; quinol inhibits the change. J. L. D.

Optically active αγ-diethylallyl alcohol. B. C. Platt (*J.C.S.*, 1941, 316—318; cf. Hills *et al.*, A., 1936, 820).—Interaction of Δ^{α}-pentenal with MgEtCl gives dl-αγ-*diethylallyl alcohol*, b.p. 58—64°/13 mm., 154—156°/760 mm., which with *o*-$C_6H_4(CO)_2O$ in C_5H_5N at 100° for 1·75 hr. gives the *H phthalate*, m.p. 66—68°. Fractional crystallisation of the *strychnine* salt, m.p. 173—178°, followed by its decomp., yields (+)- (I), m.p. 73—75°, $[\alpha]_{5461}$ +19·3° in $CHCl_3$, and (−)-αγ-*diethylallyl H phthalate*, m.p. 73—75°, $[\alpha]_{5461}$ −19·1° in $CHCl_3$, (I) with hot 5N-NaOH or 5N-EtOH–KOH gives (+)-αγ-*diethylallyl alcohol* (II), b.p. 154—156°, $[\alpha]^{18\cdot5}_{5461}$ +6·81°, which can be re-converted into (I) with little racemisation. $[\alpha]_D$ is not significantly affected by change of concn. in different solvents except in CS_2 and temp. changes have less effect than with the αγ-Me_2 analogue. (II) exhibits a slow decrease in $[\alpha]$ when kept. J. L. D.

Synthesis of asymmetrical acetylenic γ-glycols. II. A. T. Babajan (*J. Gen. Chem. Russ.*, 1940, **10**, 1177—1182).—Glycols, $OH{\cdot}CMe_2{\cdot}C{:}C{\cdot}CRR'{\cdot}OH$ (R = Me, R' = Et, Pr, n-*hexyl*, b.p. 170—172°/25 mm., *Ph*, m.p. 81°; R = R' = Ph, *Et*, m.p. 40°; RR' = *cyclo*hexyl, 4-*methyl*cyclo*hexyl*, b.p. 130—131°/22 mm.), have been prepared by the reaction $OK{\cdot}CMe_2{\cdot}C{:}CH + KOH + CORR' \rightarrow OK{\cdot}CMe_2{\cdot}C{:}C{\cdot}CRR'{\cdot}OK + H_2O$. R. T.

Conjugated systems. XI. Reaction of chloroprene with hydrogen bromide. Synthesis of γ-chloro-Δ$^{\beta}$-butenol ethers. A. A. Petrov (*J. Gen. Chem. Russ.*, 1940, **10**, 1418—1424).—CH_2:CCl·CH:CH_2 and HBr in AcOH at −5° yield *γ-chloro-α-bromo-Δ$^{\beta}$-butene*, b.p. 150—152°, which with Br in $CHCl_3$ at 0° affords *γ-chloro-αβγ-tribromobutane*, b.p. 104·5—106°, whilst hydrolysis with 10% aq. Na_2CO_3 gives OH·CH_2·CH:CMeCl (**I**) (*acetate*, b.p. 80·5—81·5°/25 mm.). With Br in $CHCl_3$ (**I**) yields *γ-chloro-αβ-dibromobutanol*, b.p. 111—112·5°/10 mm. Ethers, CMeCl:CH·CH_2·OR, are obtained from boiling solutions of (**I**) in KOR–ROH (R = Me, Et, *Pr$^{\alpha}$*, b.p. 68·5—70°/25 mm., *Bu$^{\alpha}$*, b.p. 86·7—88·5°/25 mm., *Bu$^{\beta}$*, b.p. 80—80·5°/25 mm., iso-C_5H_{11}, b.p. 98—99·5°/25 mm., *allyl*, b.p. 73—73·5°/25 mm., CH_2Ph, b.p. 137·5—138·5°/25 mm.); with KOPh a mixture of CMeCl:CH·CH_2·OPh and OH·C_6H_4·CH_2·CH:CMeCl is obtained. With NH_4CNS in MeOH (**I**) affords a thiocyanate, which undergoes isomeric change to allylcarbimide when distilled. R. T.

***n*-Heptylsulphonylacetic acid.** G. G. Urquhart and R. Connor (*J. Amer. Chem. Soc.*, 1941, **63**, 1483).—$CH_2Cl·CO_2Na$ and *n*-C_7H_{15}·SNa give *n*-C_7H_{15}·SH·CH_2·CO_2H, oxidised by H_2O_2 in AcOH–Ac_2O to *n*-heptylsulphonylacetic acid, m.p. 95·5—96° (corr.). R. S. C.

Reaction of mercuric chloride with basic lead acetate solutions. N. A. Valjaschko and G. P. Pivnenko (*J. Gen. Chem. Russ.*, 1940, **10**, 1242—1246).—The ppt. obtained when $HgCl_2$ is added to aq. Pb(OH)·OAc is represented as the complex salt $\left[Pb\langle^{OH}_{OH}\rangle Pb\langle^{OH}_{Cl}\rangle Hg\right]^{Cl}_{OH}$. R. T.

Allyl esters of certain carboxylic acids. V. P. Golendeev (*J. Gen. Chem. Russ.*, 1940, **10**, 1408—1414).—*Allyl hexoate*, b.p. 75—76°/15 mm., *palmitate*, b.p. 171—172°/3 mm., m.p. 20—21°, and *crotonate*, b.p. 88—89°/70 mm., and diallyl fumarate have been prepared from CH_2:CH·CH_2·OH and the corresponding acids, with H_2SO_4 as catalyst. *βγ-Dibromo-*, b.p. 181—182°/35 mm., and *βγ-dichloro-propyl hexoate*, b.p. 183°/68 mm., *βγ-dibromo-*, m.p. 26°, and *βγ-dichloro-propyl palmitate*, m.p. 17°, and *di-(βγ-dibromopropyl) fumarate*, m.p. 66—67°, were obtained from these esters by standard methods. R. T.

Comparative rates of oxidation of isomeric linolenic acids and their esters. J. E. Myers, J. P. Kass, and G. O. Burr (*Oil and Soap*, 1941, **18**, 107—109).—The course of oxidation (O_2 absorption) of fatty acids etc. has been studied by means of the Warburg–Barcroft respirometer. The free acids oxidise more rapidly than their esters. The max. velocities of O_2 absorption (expressed as mols. of O_2 per mol. of substance in 100 min.) were 2·68, 1·02, 0·64, 0·42, 0·52, 0·24, respectively, for α- (**I**), β- (**II**), and ψ-elæostearic [Δ^{t,tr}-octadecatrienoic acid (**III**) prepared by isomerising linseed oil acids], the Me ester of (**III**), α-linolenic acid, and Et linolenate. The influence of geometric configuration is shown by the marked difference in the oxidation velocity of (**I**) and (**II**); (**II**) and (**III**) differ less in spite of the different position of the double linkings, whilst all three require about the same time (450 min.) for the uptake of 0·5—2 mols. of O_2. Evidence was obtained that the pure acids and their esters normally show induction periods on oxidation, which are not due to the presence of inhibitors, but point to the autocatalytic nature of the oxidation process. E. L.

Fractional distillation of unsaturated fatty acids. I. Effect of vacuum distillation on the absorption spectra of polyethenoid esters from cod-liver oil. F. A. Norris, I. I. Rusoff, E. S. Miller, and G. O. Burr (*J. Biol. Chem.*, 1941, **139**, 199—206).—Determinations of absorption spectra, I vals. [Wijs $Hg(OAc)_2$ method], and sap. vals. of the products of vac. distillation of Me esters from cod-liver oil show that the heating produces some conjugation, but that the isomerised material is conc. in the residue. A. Lɪ.

Isolation of pure linoleic acid by crystallisation. J. Frankel and J. B. Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 1483—1484).—Linoleic acid, prepared from cottonseed and corn oils and purified by fractional distillation and crystallisation from $COMe_2$ and light petroleum at ≪0°, has m.p. −5·4° and Br_4 no. 100·6. Prepared from the tetrabromide and purified by crystallisation, it has m.p. −5·2° and Br_4 no. 102·3. R. S. C.

Action of sodium alkoxides on lactones. E. Y. Spencer and G. F. Wright (*J. Amer. Chem. Soc.*, 1941, **63**, 1281—1285).—No OMe-acid is obtained from γ-butyro- (**I**) or γ-valerolactone (**II**) by NaOMe (cf. Allen *et al.*, A., 1937, II, 245). The acid from (**II**) cannot be isolated directly, but neutralisation by CO_2 and acetylation (Ac_2O–C_5H_5N) gives *Me γ-acetoxy-*n*-valerate*, b.p. 88—96°/12 mm. Much divalolactone is formed, the amount being a max. when 0·5 atom of Na is used. Similar results are reported for interaction of (**I**) and (**II**) with NaOEt. Reaction mechanisms are postulated and it is concluded that lignin contains a coumarin group. *Et γ-acetoxy-*n*-valerate*, b.p. 118—125°/16 mm., and *-butyrate*, b.p. 102·5°/13 mm., are described. R. S. C.

Reactions of ethylene oxide. (A) Condensation with substituted malonic esters. (B) Condensation with ethyl acetoacetate. K. Packendorf and F. F. Matschus (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **29**, 577—578, 579—581).—(A) $CHEt(CO_2Et)_2$ and *iso*-C_5H_{11}·$CH(CO_2Et)_2$ with $(CH_2)_2O$ and $C_5H_{11}N$ yield respectively *α-carbethoxy-α-ethyl-*, b.p. 124°/10 mm., and *-isoamyl-butyrolactone*, b.p. 120—130°/9 mm., hydrolysed and decarboxylated (10% H_2SO_4) to α-ethyl- and *-iso*amyl-butyrolactone.

(B) $CH_2Ac·CO_2Et$ with $(CH_2)_2O$ and $C_5H_{11}N$ yields a mixture of α-(β-hydroxyethyl)butyrolactone and its acetate. A. Lɪ.

Products of condensation of α-formylcarboxylic acid esters with α-halogen-substituted esters. II. Carboxylation of vinyl alkyl esters. M. N. Schtschukina and N. A. Preobrashenski (*J. Gen. Chem. Russ.*, 1940, **10**, 1363—1368).—Et sodio-α-formylpropionate in EtOH and $CH_2Cl·CO_2Et$ (5 hr. at the b.p.) yield the *ether*, $CO_2Et·CMe$:CH·O·CH_2·CO_2Et, b.p. 147—149°/12 mm., which when hydrolysed with 1% $H_2C_2O_4$ gives EtCHO and OH·CH_2·CO_2H; mild hydrolysis with NaOEt in EtOH affords CHO·CHMe·CO_2H. Et_2 sodio-α-formyl-β-ethylsuccinate and CHEtBr·CO_2Et are condensed as above, to give the *ester*, $CO_2Et·CHEt·C(CO_2Et)$:CH·O·CHEt·CO_2Et (**I**), b.p. 200—202°/12 mm., hydrolysed by NaOEt in EtOH to the corresponding tricarboxylic acid. This eliminates CO_2 in acid solution, yielding the *acid*, $CO_2H·CHEt·CH$:CH·O·CHEt·CO_2H, m.p. 148—150°, b.p. 178—198°/11 mm. (*lactone*, b.p. 204—207°/11 mm.). Hydrolysis of (**I**) with HCl gives CHO·CH_2·CHEt·CO_2H and OH·CHEt·CO_2Et. The ether $CO_2Et·CH_2·C(CO_2Et)$:CH·O·CHEt·CO_2Et hydrolysed with 1% $H_2C_2O_4$ or NaOEt in EtOH affords the *acid*, $CO_2H·CH_2·CH$:CH·O·CHEt·CO_2H, which when distilled gives the *lactone*, b.p. 195—197°/14 mm. Hydrolysis of $CO_2Et·CHEt·C(CO_2Et)$:CH·O·CH_2·CO_2Et with 1% $H_2C_2O_4$ affords the tricarboxylic *acid* $CO_2Et·CHEt·CH$:CH·O·CH_2·CO·O·CH(O·CH_2·CO_2H)·CH_2·CHEt·CO_2H, m.p. 102—103°. R. T.

Resolution of *dl*-α-hydroxy-ββ-dimethyl-γ-butyrolactone. R. T. Major and J. Finkelstein (*J. Amer. Chem. Soc.*, 1941, **63**, 1368—1371).—*dl*-α-Hydroxy-ββ-dimethyl-γ-butyrolactone and the appropriate alkaloid methohydroxide in H_2O at room temp. give, after evaporation, *quinine*, m.p. 176—177°, $[\alpha]_D^{25}$ −160·56° in H_2O, *cinchonine*, m.p. 189—190°, $[\alpha]_D^{25}$ +179·5° in H_2O, and *quinidine metho-αγ-dihydroxy-ββ-dimethylbutyrate*, m.p. 153—154°, $[\alpha]_D^{24}$ +213·91° in H_2O, also obtained from the *l*-lactone. Separation of quinidine (**I**) (*methochloride*, m.p. 236—237°, $[\alpha]_D^{25}$ +257·9° in H_2O) and dihydroquinidine from commercial (**I**) by $Hg(OAc)_2$ etc. is described. R. S. C.

Products of chemical and biochemical decomposition of ascorbic acid. I. Titrimetric acidity and oxygen consumption in chemical decomposition. E. A. Scheinkman (*Ukrain. Biochem. J.*, 1940, **15**, 151—167).—The decomp. of ascorbic acid (**I**) in alkaline solution into $H_2C_2O_4$ and *l*-tetronic acid (cf. A., 1933, 1143) is confirmed by titration [3 mols. of NaOH per mol. of (**I**) are required] and by determination of the O_2 consumed [1 mol. per mol. of (**I**)] during the oxidation. J. N. A.

Exchange of oxalates of complex trioxalate ions of tervalent metals.—See A., 1941, I, 343.

Furanose and pyranose derivatives of glucurone. L. N. Owen, S. Peat, and W. J. G. Jones (*J.C.S.*, 1941, 339—344).—Glucuronolactone (glucurone) in 0·5% HCl–MeOH at room temp. for 3 days, followed by treatment with Ag_2CO_3, gives the *γ-lactone* (**I**), m.p. 139°, $[\alpha]_D^{18}$ −57° in H_2O, of *β-methyl-glucofururonoside*, which gave no absorption bands in H_2O but in dil. alkali showed bands at 2790 and 4160 A.; the latter disappeared on acidification and re-appeared when the

solution was made alkaline. (I) shows no mutarotation and titration with 0·1N-NaOH shows it to be a γ-lactone. Thorough methylation of (I) in $COMe_2$ with Ag_2O–MeI, followed by treatment with cold 0·3N-$Ba(OH)_2$ for 20 min., and regeneration of the lactone after removing any ester present, gives the *γ-lactone* (II), b.p. 150° (bath)/0·01 mm., of 2 : 5-*dimethyl-β-methylglucofururonoside*, converted by MeOH–NH_3 at 0° into the *amide*, m.p. 95°. (II) when methylated with Me_2SO_4 in aq. $COMe_2$–NaOH gives 2 : 3 : 5-*trimethyl-β-methylglucofururonoside*, an oil, which after treatment with 3% HBr at 90° for 8 hr. followed by oxidation (Br) and esterification (boiling 2% HCl–EtOH) gives 2 : 3 : 5-trimethylsaccharolactone Me ester, m.p. 77—78°. (I) with MeOH–NH_3 at 0° gives the *amide* of *β-methylglucofururonoside*, an oil, which gives a positive Weerman reaction. (I) with boiling 2% HCl–MeOH for 6 hr. gives the *Me* ester of *methylglucopyrururonoside* (III), a non-reducing syrup, which contains 1 Me easily replaceable by alkalis. When thoroughly methylated (Ag_2O–MeI) (III) gives the *Me* ester of 2 : 3 : 4-*trimethylmethylglucopyrururonoside*, b.p. 120° (bath)/0·02 mm. $[\alpha]_D^{17}$ +84° in MeOH, converted by MeOH–NH_3 into the amide of 2 : 3 : 4-trimethyl-α-methylglucuronoside. Glucuronolactone in dry $COMe_2$ containing conc. H_2SO_4 gives 1 : 2-*isopropylidineglucofururono-γ-lactone* (IV), m.p. 120°, $[\alpha]_D^{18}$ +70°, which with alkali behaves like a δ-lactone, yields CHI_3 with alkaline hypoiodite, and shows similar absorption spectra to those of (I). (IV) when thoroughly methylated (Ag_2O–MeI) gives 2 : 5-dimethyl-2 : 3-dehydrosaccharolactone Me ester, m.p. 89°, $[\alpha]_D$ +89° in MeOH (cf. Pryde *et al.*, A., 1933, 1035; Schmidt *et al.*, A., 1938, II, 42). 1 : 2-*iso*Propylideneglucofururonic acid (V) (cf. Zervas *et al.*, A., 1933, 1143) when heated at 95—100°/0·01 mm. for 1 hr. gives (IV). (IV) in dry MeOH containing NH_3 at 0° in 24 hr. gives 1 : 2-iso*propylideneglucofururonamide*, m.p. 164° (decomp.), $[\alpha]_D^{18}$ −14° in H_2O [also obtained by treatment of the Me ester of (V) with MeOH–NH_3 at 0° for 36 hr.], which gives a positive Weerman reaction.

J. L. D.

Chemoimmunological studies on the soluble specific substance of pneumococcus. V. Structure of type III polysaccharide. R. E. Reeves and W. F. Goebel (*J. Biol. Chem.*, 1941, **139**, 511—519).—Methylation (Me_2SO_4) of the polysaccharide (I) of type III pneumococcus yields the *compound* $[C_{11}H_{12}O_4(OMe)_5{\cdot}CO_2H]_n$, $[\alpha]_D^{24}$ −35·8° in $CHCl_3$–EtOH (4 : 1), the *Me* ester (CH_2N_2), m.p. 185—200°, $[\alpha]_D^{23}$ −36·8° in $CHCl_3$, of which is reduced (Ba–Cu chromite at 175° under pressure) to the corresponding *OH*-compound, $[C_{17}H_{30}O_{10}]_n$, $[\alpha]_D^{23}$ −15·6° in $CHCl_3$. Hydrolysis (dil. HCl) of this yields 2 : 3 : 6-trimethylglucose and 2 : 4-*dimethyl-α-* (II), m.p. 79—81°, $[\alpha]_D^{20}$ +159° in $COMe_2$ (also obtained from 6-triphenylmethyl-α-methylglucoside; cf. Robertson *et al.*, A., 1931, 1040), and -β-methylglucoside (III). (II) with MeOH–HCl at 100° yields (III). Mixed (II) and (III) with $NHPh{\cdot}NH_2$,HCl and NaOAc yield 4-methylglucosazone. Acid hydrolysis of (I), when glucosidic, but not when glucuronosidic linkings are attacked, gives a *d*-solution. It is concluded that in the mol. of (I), glucose is linked to $C_{(3)}$ of glucuronic acid, and this (β-linking) to $C_{(4)}$ of a second glucose mol.

A. Li.

Preparation of aldehydes and ketones.—See B., 1941, **II**, 213.

Influence of peracetic acid on the cold-flame oxidation of acetaldehyde.—See A., 1941, I, 340.

Photochemical decomposition of acetone in presence of hexadeuterodiacetyl.—See A., 1941, I, 342.

Hexadeuterodiacetyl.—See A., 1941, **I**, 342.

Crystalline β-methyl-*D*-ribopyranoside. E. L. Jackson and C. S. Hudson (*J. Amer. Chem. Soc.*, 1941, **63**, 1229—1231).—Methyl-*D*-riboside (prep. described; cf. Minsaas, A., 1934, 1091), m.p. 83°, [α] −105·0° in H_2O, and HIO_4 give *L'*-methoxydiglycolldialdehyde and thence Sr *L'*-methoxydiglycollate and is thus β-methyl-*D*-ribopyranoside.

R. S. C.

Reaction capacity of physiologically important substances in mixtures. III. Reactions of simple sugars in presence of glycine. A. Kuzin and Z. Makaeva (*Biochimia*, 1939, **4**, 367—372).—The reducing power of monoses is increased in presence of small amounts of glycine (I), but with increase of the latter the reducing power is decreased, becoming zero with a saturated solution of (I). Possibly unstable compounds of (I) and the monoses are formed that, in presence of small amounts of (I), are decomposed with liberation of enolised sugar derivatives which cause the activation effect. With conc. solutions of (I), removal of (I) from the compound is inhibited, and no reducing groups are liberated.

J. N. A.

Derivatives of the aldehydrol form of sugars. IV. M. L. Wolfrom and R. L. Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 1246—1247; cf. A., 1940, II, 364).—*aldehydo-d*-Galactose penta-acetate and a little $ZnCl_2$–AcOH in AcCl give α-1-*chloro*-aldehydo-d-*galactose hexa-acetate*, m.p. 153—154°, $[\alpha]_D^{22}$ +62° in $CHCl_3$, $[\alpha]_D^{23}$ +60° in AcCl, and a little of the known β-isomeride, $[\alpha]_D^{22}$ −47° in AcCl. These isomerides are equilibrated (76·5% α-) by $ZnCl_2$–AcCl, changes in [α] determining the configurations stated.

R. S. C.

Active form of monosaccharides. VI. Reactivity of fructose 1-phosphate. A. V. Stepanov and B. N. Stepanenko (*Biochimia*, 1940, **5**, 198—207; cf. A., 1938, II, 83).—The prep. of pure Ba fructose 1-phosphate (I) from β-di*iso*propylidenefructose is described. Cyanohydrin formation occurs more readily with (I) than with fructose. The bearing of the increased reaction capacity of (I) on its structure is discussed.

F. O. H.

***D*-Glucosan<1,5>β<1,6> and *D*-galactosan <1,5>β<1,6> from the pyrolysis of lactose.** R. M. Hann and C. S. Hudson (*J. Amer. Chem. Soc.*, 1941, **63**, 1484—1485).—Pyrolysis of commercial agar and treatment of the product with $COMe_2$–$CuSO_4$ (cf. following abstract) gives 0·2—1·4% of *iso*propylidene-*D*-galactosan (I), m.p. 151—152°, $[\alpha]_D^{20}$ −72·9° in $CHCl_3$. α-Lactose, $+H_2O$, gives similarly excellent yields of *D*-galactosan<1,5>β<1,6> (II), m.p. 223—224° (corr.), $[\alpha]_D^{20}$ −22·0° in H_2O, and *D*-glucosan <1,5>β<1,6>, readily separated by way of (I). The structure of (II) is proved by HIO_4-oxidation.

R. S. C.

***D*-Mannosan<1,5>β<1,6> or *l*-mannosan.** A. E. Knauf, R. M. Hann, and C. S. Hudson (*J. Amer. Chem. Soc.*, 1941, **63**, 1447—1451).—Pyrolysis (apparatus described) of vegetable ivory meal (*Phytelephas macrocarpa*, Ruiz and Pav.) and treatment of the H_2O-sol., syrupy portion of the distillate with $COMe_2$ and anhyd. $CuSO_4$ gives 8·3% of 2 : 3-iso*propylidene*-D-*mannosan*<1,5>β<1,6> (I), m.p. 161—162°, [α] (in this and other cases $[\alpha]_D^{20}$) −58·8° in H_2O, hydrolysed by 0·1N-H_2SO_4 at 20° to *D*-mannosan<1,5>β<1,6> (II), m.p. 210—211°, [α] −127·6° in H_2O. Structures are proved as follows: (*a*) with hot N-HCl, (I) or (II) give almost quantitatively *D*-mannose and with 5% HCl–MeOH gives α-methyl-*D*-mannopyranoside; (*b*) 2 mols. of HIO_4 are reduced by (II), giving 1 mol. each of HCO_2H and dialdehyde, oxidised as usual to Sr *L'*-oxy-*D*-methyleneglycollate. (I) gives 2 : 3-iso*propylidene*-D-*mannosan*<1,5>β<1,6> 4-*acetate*, m.p. 101—102°, [α] −72·2° in $CHCl_3$, 4-*benzoate*, m.p. 134—135°, [α] −103·5° in $CHCl_3$, and 4-p-*toluenesulphonate*, m.p. 144—145°, [α] −39·8° in $CHCl_3$, and (by MeI–Ag_2O–$COMe_2$) 4-*methyl*-2 : 3-iso*propylidene*-D-*mannosan*<1,5>β<1,6>, m.p. 53—54°, [α] −33·4° in $CHCl_3$, which with hot N-HCl gives 4-methyl-*D*-mannose, [α] +18·8° (phenylosazone, m.p. 158—159°, [α] −36·0° → −14·4° in EtOH in 24 hr.). *D*-Mannosan <1,5>β<1,6> 2 : 3 : 4-triacetate, m.p. 90—91° (lit. 86°), [α] −123·6° in $CHCl_3$, *-tribenzoate*, m.p. 111—112°, [α] −185·2° in $CHCl_3$, and *-tri*-p-*toluenesulphonate*, m.p. 207—208°, [α] +29·7° in $CHCl_3$, are prepared in C_5H_5N. M.p. are corr.

R. S. C.

Decomposition of hexoses to hydroxymethylfurfuraldehyde. A. D. Braun (*Biochimia*, 1939, **4**, 276—282).—The formation of hydroxymethylfurfuraldehyde from ketohexoses is catalysed by acids, whilst the similar transformation of aldohexoses requires the presence of both acid and base. Alkali transforms the aldohexose into the epimeric ketose, which is then converted by the acid into the aldehyde derivative.

J. N. A.

2-Methyl-1 : 4-naphthaquinol di-β-*D*-glucoside. B. Riegel, P. G. Smith, and C. E. Schweitzer (*J. Amer. Chem. Soc.*, 1941, **63**, 1231—1232).—2-Methyl-1 : 4-naphthaquinol with α-*D*-glucosyl bromide tetra-acetate, KOH, and $Na_2S_2O_4$ in $COMe_2$–N_2 or β-*D*-glucose penta-acetate with *p*-$C_6H_4Me{\cdot}SO_3H$ at 130° gives 21·5 and 2·8—5%, respectively, of 2-*methyl*-1 : 4-*naphthaquinol di-(β*-D-*glucoside tetra-acetate)*, m.p. 212—213°, $[\alpha]_D^{25}$ −32±2° in $CHCl_3$, hydrolysed by $Ba(OH)_2$ at room temp. or (93% yield) hot NH_3–MeOH to the free *diglucoside* (I), $+H_2O$, m.p. 275° (decomp.), $[\alpha]_D^{25}$ −61±1° in 50% $COMe_2$. (I) is only slightly sol. (0·1—0·2 mg. per ml.) but readily gives supersaturated solutions and is thus shown to have approx. one third (wt./wt.) of the vitamin-*K* activity of the quinol. The dimannoside could not be obtained.

R. S. C.

Starch molecule.—See A., 1941, I, 327.

Preparation of derivatives of starch. E. Pacsu and J. W. Mullen, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 1487—1488).—Bursting the granules of native starch, *e.g.*, by boiling H_2O, boiling in C_5H_5N, and boiling off the C_5H_5N–H_2O azeotrope gives a solution (*A*) which is clear if it contains ~4% of H_2O and gels if anhyd. Tri-esters are readily prepared from (*A*). R. S. C.

Molecular size of polysaccharides [determined] by the mercaptalation method. Methylated potato starch. M. L. Wolfrom and D. R. Myers (*J. Amer. Chem. Soc.*, 1941, **63**, 1336—1339).—The mercaptalation method (A., 1939, II, 301) (which is independent of branching), applied to methylated potato starch (**I**) (method of prep.: Hess and Lung, A., 1938, II, 221), hydrolysing at 0°, shows the average degree of polymerisation to vary from 34 glucose units after 1·5 hr. to 3 after 20·55 hr.; $k = 2{\cdot}22 \times 10^{-6}$, similar to that for unmethylated potato starch (A., 1939, II, 494). Extrapolation shows initial $[\alpha]_D^{20}$ + 212·5° for (**I**) and an initial average degree of polymerisation = ⩽150, although η in $CHCl_3$ at 20° indicates that the latter = 7000. Thus, the 25 glucose units indicated by other methods as a fundamental unit for starch do not represent the whole mol. R. S. C.

Synthesis of chloroalkyldialkylamines. H. B. Hass and H. C. Huffman (*J. Amer. Chem. Soc.*, 1941, **63**, 1233—1235).—Chlorination (apparatus described) of n-$C_5H_{11}Cl$ gives αα- + αβ- 20, αγ- (b.p. 80·4°/60 mm.) 30, αδ- (b.p. 88·1°/60 mm.) 31, and αε-dichloropentane (b.p. 102·4°/60 mm.) 19, and polychlorides 44%. The ease of reaction of Cl in dichlorides with NaI in anhyd. $COMe_2$ is $CH_2Cl > CHCl > CCl$. Thus, the appropriate dichloride with 1·0—1·1 mol. of NaI gives $Cl{\cdot}[CH_2]_3{\cdot}I$ (53·1%), b.p. 60·8°/15 mm., $CHMeCl{\cdot}[CH_2]_2{\cdot}I$ (77·8%), b.p. 51·4°/6·5 mm., $CHEtCl{\cdot}[CH_2]_2{\cdot}I$ (90·4%), b.p. 50·5°/2·5 mm., $CHMeCl{\cdot}[CH_2]_3{\cdot}I$ (**I**) (90·0%), b.p. 61·3°/3·5 mm., and $Cl{\cdot}[CH_2]_5{\cdot}I$ (61·6%), b.p. 75·8°/4 mm., with smaller amounts of $I{\cdot}[CH_2]_3{\cdot}I$, b.p. 78·5°/5 mm., $CHMeI{\cdot}[CH_2]_2{\cdot}I$, b.p. 80—82°/5 mm., $CHEtI{\cdot}[CH_2]_2{\cdot}I$, b.p. 80—82°/2·5 mm., $CHMeI{\cdot}[CH_2]_3{\cdot}I$, b.p. 100°/5 mm., and $I{\cdot}[CH_2]_5{\cdot}I$, b.p. 101—102°/3 mm. The iodochloride with $NHEt_2$ (3—4 mols.) at room temp. gives 42—74% of diethyl-γ-chloropropyl-, m.p. 85·8—86·2°, -γ-chlorobutyl-, m.p. 83—84°, -γ-chloro-*n*-amyl-, m.p. 98·5°, -δ-chloro-*n*-amyl-, m.p. 99·0°, and -ε-chloro-*n*-amyl-, m.p. 80—81°, -amine hydrochloride. NaI, $NHEt_2$, and (**I**) give a mixture containing much 2-methyl-1-ethylpyrrolidine ethochloride. R. S. C.

Ammonolysis. I. Ammonolysis of halogen fatty acids and preparation of α-amino-acids. N. D. Cheronis and K. H. Spitzmueller (*J. Org. Chem.*, 1941, **6**, 349—375).—Ammonolysis of halogen acids ($CH_2Cl{\cdot}CO_2H$, $CH_2Br{\cdot}CO_2H$, $CHMeCl{\cdot}CO_2H$, $CHMeBr{\cdot}CO_2H$, $CHEtBr{\cdot}CO_2H$, $CHPr^{\alpha}Br{\cdot}CO_2H$, $CHPr^{\beta}Br{\cdot}CO_2H$, and $CHBu^{\alpha}Br{\cdot}CO_2H$) at 60° with 4—6 mols. of $(NH_4)_2CO_3$ gives about the same amounts of NH_2-acids as 60 mols. of aq. NH_3 at 60°. With varying mol. ratios of acid to NH_3 increase in the concn. of NH_3 produces an increase in the yield of glycine (**I**) from $CH_2Cl{\cdot}CO_2H$ at 25°, 40°, and 50°; at 60°, 70°, and 100° the effect of increased concn. drops abruptly after a 1 : 12 mol. ratio of acid to NH_3 has been reached. At 25° and at 60° the presence of various NH_4 salts increases the conversion of $CH_2Cl{\cdot}CO_2H$ into (**I**); $(NH_4)_2CO_3$ gives the max. effect. Investigation of the p_H of various ammonolytic media, of the composition of $(NH_4)_2CO_3$ solutions, and of the rates between $CH_2Cl{\cdot}CO_2H$ and (**I**) shows that the formation of *sec.*- and *tert.*-NH_2-compound can be inhibited by lowering the p_H of the ammonolytic medium and by the formation of an unstable NH_2-acid carbamate. The p_H and carbamate effects are of general application in ammonolytic reactions; the optimum conditions of the ammonolysis of halogen acids for the prep. of NH_2-acids are described. H. W.

Reaction capacity of physiologically important organic substances in mixtures. IV. Reaction capacity of ethyl ester of glycine in presence of carbonyl compounds. A. M. Kuzin and O. I. Poljakova (*Biochimia*, 1940, **5**, 86—92).—Simple sugars, acting as catalysts, increase the yield of diketopiperazine from $NH_2{\cdot}CH_2{\cdot}CO_2Et$ by 100%, whereas MeCHO, CH_2O, $COMe_2$, or compounds similar to sugars without CO (*e.g.*, mannitol) have no effect. This is probably due to activation of the NH_2 by formation of an unstable intermediate compound. H. G. R.

Reaction of ethyl glycinate hydrochloride with primary, secondary, and tertiary Grignard reagents. F. L. Greenwood and R. A. Gortner (*J. Org. Chem.*, 1941, **6**, 401—409).—Contrary to earlier workers, the conversion of NH_2-esters into their hydrochlorides does not protect the NH_2 group from the Grignard reagent. In all the reactions studied gases are evolved in large amount. Apparently all three H attached to N are active and completely displaced by the Grignard reagent if the reaction mixture is warmed for a sufficient time. The only hydrocarbon found is that corresponding with the Grignard reagent used. Large excesses of reagent are necessary to secure good yields. $NH_2{\cdot}CH_2{\cdot}CO_2Et$,HCl (**I**) is transformed by $MgPr^{\alpha}Cl$ in anhyd. Et_2O into $NH_2{\cdot}CH_2{\cdot}CPr^{\alpha}_2{\cdot}OH$, b.p. 76°/4 mm., m.p. 41·5° (lit. m.p. 58°) (*hydrochloride*, m.p. 106·5—107·5°; *Bz* derivative, m.p. 91—91·2°); the gas evolved contains 57·2% of C_3H_8 and 38·8% of matter nor condensable in liquid O_2 but CO, CO_2, O_2, and olefines do not appear to be present. Similarly (**I**) and $MgPr^{\beta}Cl$ afford β-amino-αα-di*iso*propylethanol (*hydrochloride*, m.p. 196—197°; *SO_2Ph* derivative, m.p. 103·9—104·5°) and $NH_2{\cdot}CH_2{\cdot}COPr^{\beta}$ [*hydrochloride*, m.p. 147—149° (decomp.) after becoming discoloured at 145°; *SO_2Ph* derivative, m.p. 81°]; C_3H_8 and uncondensable matter are evolved. The only products isolable from (**I**) and $MgBu^{\gamma}Cl$ are *iso*butane and uncondensable matter. H. W.

Action of sodium selenite on the oxidation of *l*-proline. F. Bernheim and J. R. Klein (*J. Biol. Chem.*, 1941, **139**, 827—833; cf. Wright, A., 1940, III, 347).—Small concns. of Na_2SeO_3 immediately inhibit the oxidation of *l*-proline by liver, inhibit after a latent period the oxidation of succinate, choline, *d*-proline, or tyramine by liver, and have little or no effect on the oxidation of *l*-tyrosine, xanthine, or EtOH by liver, or of glucose, lactate, or pyruvate by brain. Liver oxidations are inhibited by shaking with Na_2SeO_3 before addition of substrate. Large quantities of arsenite, molybdate, chromate, permanganate, and metavanadate have no effect on the oxidation of *l*-proline. A. Li.

Synthesis of *dl*-citrulline from non-biological precursors. S. W. Fox, M. S. Dunn and M. P. Stoddard (*J. Org. Chem.*, 1941, **6**, 410—415).—*cyclo*Pentanone is converted by $(NH_2OH)_2,H_2SO_4$ into its oxime, b.p. 93—97°/24 mm., m.p. 53·5—54·5° (yield 93%), re-arranged by boiling ~30N-H_2SO_4 to 2-piperidone. This with 2·5N-H_2SO_4 followed by BzCl and NaOH affords $NHBz{\cdot}[CH_2]_4{\cdot}CO_2H$ (**I**), m.p. 90°±1°, in 71% yield. (**I**) is transformed by successive treatments with Br–red P in dry CCl_4, $NaHCO_3$, HCl, and 15N. aq. NH_3 into *dl*-δ-benzoylornithine, hydrolysed by boiling HCl to ornithine hydrochloride. This is converted by CuO in boiling H_2O followed by $CO(NH_2)_2$ into Cu *dl*-citrullinate and thence by H_2S into *dl*-citrulline [α-amino-δ-carbamido-*n*-valeric acid]. H. W.

Resolution of racemic pantothenic acid by means of quinine methohydroxide. E. T. Stiller and P. F. Wiley (*J. Amer. Chem. Soc.*, 1941, **63**, 1237—1239).—*dl*-Pantothenic acid is resolved by quinine methohydroxide in H_2O at 0°. Cinchonidine yields the (+)-acid [*cinchonidine* salt (**I**), m.p. 177—178°, $[\alpha]_D^{25}$ −61·3° in MeOH]. *Quinine metho*-(+)- (**II**), m.p. 196—197°, $[\alpha]_D$ −118·5° in MeOH, and -(−)-*pantothenate* (**III**), m.p. 170°, $[\alpha]_D^{25}$ −156·0° in MeOH, are described. (**I**) and (**II**) have full biological activity, but (**III**) has very little. R. S. C.

Spatial configuration and preparation of canavanine. J. F. Cadden (*Proc. Soc. Exp. Biol. Med.*, 1940, **45**, 224—226).—The prep. of dextrorotatory canavanine (**I**), m.p. 171° (decomp.) (lit., decomp. 182°), from jack-been meal by way of the *flavianate*, decomp. 218—220°, (purification described), and sulphate, decomp. 172°, is described. Application of the method of Lutz and Jirgensons (A., 1930, 460) to (**I**) showed a decided shift of $[\alpha]_D$ towards the positive with increasing [HCl]; (**I**) should therefore be designated *l*(+)-canavanine. V. J. W.

Crystalline amino-acid complex from *Astragalus pectinatus*.—See A., 1941, III, 713.

Esters of phosphoric acid. IV. Phosphorylhydroxyamino-acids. R. H. A. Plimmer (*Biochem. J.*, 1941, **35**, 461—469).—The following were prepared by heating the appropriate NH_2-acids with $H_3PO_4 + P_2O_5$ to 100°; phosphotyrosine, m.p. 225°, $[\alpha]_D$ −9·19° in 2N-HCl (cf. Levene and Schorlmüller, A., 1933, 607); phosphohydroxyproline, m.p. 115°,

$[\alpha]_D$ −28·76° in H_2O (cf. A., 1934, 1208); phosphoserine, m.p. 165—166° (decomp.) (cf. A., 1934, 876); phospho*iso*serine; *phosphothreonine*, m.p. 169° (decomp.) (*Pb* and *Ba* salts). Hydroxyaspartic acid cannot be phosphorylated in this way even at 20 lb. pressure. All the esters are hydrolysed by animal phosphatases or by N-HCl at 100°, but are stable to N-NaOH at 37°; only phospho*iso*serine is not hydrolysed by N-NaOH at 100°. P. G. M.

Azlactones. IV. Synthesis of α-amino-β-thiol-*n*-butyric acids. H. E. Carter, C. M. Stevens, and L. F. Ney (*J. Biol. Chem.*, 1941, **139**, 247—254).—α-Benzamidocrotonic acid azlactone I (A., 1940, II, 172) or *Me* α-*benzamidocrotonate* I, m.p. 78—80°, with $CH_2Ph{\cdot}SH$ and NaOMe, followed by hydrolysis (AcOH–dil. HCl), yields mixtures (in proportions depending on conditions) of the dl-N-*Bz* derivatives, m.p. 145—147° (**I**) and 181—187° (**II**) (β-phenylethylamine salts, m.p. 166—168° and 147—150°, respectively) (hydrolysed by aq. HCl–HCO_2H), of *α-amino-β-benzylthiol-*n*-butyric acids* A and B, m.p. 197—199° (decomp.) and 202—204° (decomp.), respectively, reduced (Na in liquid NH_3) to *α-amino-β-thiol-butyric acids* A and B, m.p. 203—205° (decomp.) (**III**) and 203—204° (decomp.) (**IV**), respectively. These are reconverted by CH_2PhCl and Na in liquid NH_3, followed by BzCl and NaOH, into (**I**) and (**II**), respectively. (**IV**) gives the same intensity of colour as cysteine with Lugg's modification of Sullivan's test for cystine, (**III**) only 20% as much. A. Lt.

Synthesis of lipophilic chemotherapeuticals. III. Properties of halogeno-acylcarbamides, -carbamides, and related compounds. F. Bergmann and L. Haskelberg (*J. Amer. Chem. Soc.*, 1941, **63**, 1437—1439; cf. A., 1940, II, 262).—Introduction of Cl into the Ac of NH_2Ac, $NH_2{\cdot}CO{\cdot}NHAc$, NHPhAc, *o*-$OAc{\cdot}C_6H_4{\cdot}CO_2H$, etc. increases the toxicity (intraperitoneal injection), the Cl_4-derivatives being the most toxic (except that di- is more toxic than mono- or tri-chloroacetylcarbamide). The effect of Cl is less than that of Br. $NHPh{\cdot}CO{\cdot}CCl{:}CCl_2$ is not particularly effective. The following are prepared. $CCl_2{:}CCl{\cdot}CO{\cdot}NH_2$, m.p. 87° (lit. 20°), $CCl_3{\cdot}CCl_2{\cdot}CHCl_2$ (from C_2Cl_4, $CHCl_3$, and $AlCl_3$ at −10° and later 100°), m.p. 30°, b.p. 122°/25 mm., and thence (25% KOH–MeOH) C_3Cl_6, b.p. 100°/45 mm., 210°/759 mm., and [H_2SO_4–$Al_2(SO_4)_3$; 110—130°] $CCl_2{:}CCl{\cdot}CO_2H$, m.p. 76° (*anilide*, m.p. 98°). *ικ-Dibromoundecoylcarbamide*, m.p. 161°. Chloro-, m.p. 134—135° (lit. an oil), *dichloro-*, m.p. 126—127°, and *trichloro-acetylsalicylic acid*, m.p. 138—139°. R. S. C.

Urea synthesis.—See B., 1941, II, 214.

Dipole moment and bond character in organometallic compounds. C. P. Smyth (*J. Org. Chem.*, 1941, **6**, 421—426).—Use of the dipole moments of org. mols. containing Hg, Ge, Sn, Pb, or Sb and Cl, Br, or I to determine the approx. amounts of ionic character in the bonds linking the atoms to one another in conjunction with data from the literature shows that the linkings between C and metal atoms are essentially covalent. Those connecting metal atoms to Cl, Br, or I in the same compound are as ionic in character as the linkings in some typical salt mols. supposed to consist of a pair of oppositely charged ions. H. W.

Reaction of α-halogenocarbonyl compounds with Grignard reagents. I. R. C. Huston, R. I. Jackson, and G. B. Spero (*J. Amer. Chem. Soc.*, 1941, **63**, 1459—1460).—$CHMePr^{\beta}{\cdot}OH$ is obtained from $CH_2Cl{\cdot}COCl$, $CH_2Br{\cdot}COBr$, $CH_2Cl{\cdot}CO_2Et$, or $CH_2Br{\cdot}CO_2Et$ by MgMeI (4 mols.) and (20%) from $COMe{\cdot}CH_2Br$ by MgMeBr or MgMeI (2 mols.). R. S. C.

Synthesis of keto-acids and ketones by the reaction of acid anhydrides with cadmium alkyls. P. L. de Benneville (*J. Org. Chem.*, 1941, **6**, 462—466).—Ketones and CO-acids are obtained from non-cyclic and cyclic anhydrides with Cd dialkyls and diaryls. The yields are more satisfactory than those obtained from anhydrides and Grignard reagents and the method is more generally applicable than the Friedel–Crafts synthesis with the added advantage of predictable orientation of groups in the product. The Cd alkyls are prepared by addition of anhyd. $CdCl_2$ to the appropriate Grignard reagent in Et_2O and the anhydride is slowly added as liquid, in Et_2O, or as solid, at 0°. After being gently boiled for 1—1½ hr. the mixture is decomposed with 10% H_2SO_4. Any ester is removed from the ketonic product by hydrolysis. Reactions with the following initial products are described: *o*-$C_6H_4(CO)_2O$ and MeBr, MeI, EtBr, PhBr, and I-$C_{10}H_7Br$; $(CH_2{\cdot}CO)_2O$ and PhBr; Ac_2O and $Bu^{\alpha}Br$ or PhBr; $(EtCO)_2O$ and PhBr; $(Pr^{\beta}CO)_2O$ and PhBr; Bz_2O and EtBr, $Pr^{\alpha}Br$, $Pr^{\alpha}I$, and $Bu^{\gamma}Cl$. H. W.

II.—HOMOCYCLIC.

Isomerisation of polymethylenic hydrocarbons in presence of aluminium chloride. VI. *iso*Propyl*cyclo*pentane. M. B. Turova-Poljak and T. A. Slovochotova (*J. Gen. Chem. Russ.*, 1940, **10**, 1435—1438).—When heated with $AlCl_3$ at 125—130° *iso*propyl*cyclo*pentane affords an equilibrium mixture of paraffins 2·9, *cyclo*pentanes 9·4, and 1 : 3- and 1 : 4-dimethyl-*cyclo*hexane 87·7%; the same products are obtained from *n*-propyl*cyclo*pentane. R. T.

Vanadium oxides as hydrogenation and dehydrogenation catalysts. G. D. Lubarski and M. J. Kagan [in part with G. L. Natanson] (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **29**, 575—576).—In presence of Al_2O_3 coated with V_2O_5, previously reduced at 550—600° for 2—3 hr., *cyclo*hexane at 475° yields C_6H_6 (20%), C_4H_{10} at 575° yields C_4H_8 (82—88%), and PhEt at 630° yields styrene (75—80%). Lower yields are obtained with Al_2O_3 alone. A. Lt.

Catalytic dehydrogenation of hydroaromatic compounds with benzene. H. Adkins, L. M. Richards, and J. W. Davis (*J. Amer. Chem. Soc.*, 1941, **63**, 1320—1325).—Aromatic compounds are obtained from hydroaromatic hydrocarbons, alcohols, ketones, and ethers (28 examples) by heating at 300—350° under N_2 (150 atm.) in presence of Pt or various forms of Ni. The nature of the products (hydrocarbons, phenols, and condensation products) depends somewhat on the catalyst. Ni on Al_2O_3 or kieselguhr is often the most active catalyst and gives best yields of phenols. Pt is occasionally effective at a lower temp. but converts *cyclo*hexanols into aromatic hydrocarbons. Details of yields are given. R. S. C.

Alkylation of aromatic compounds by means of alcohols in presence of anhydrous ferric chloride. Z. N. Nazarova and I. P. Tzukervanik (*J. Gen. Chem. Russ.*, 1940, **10**, 1151—1155).—*iso*-Alcohols readily condense with aromatic hydrocarbons in presence of anhyd. $FeCl_3$. The reactivity of the alcohols rises in the order primary < *sec.* < *tert.*, as is indicated by the yields and temp. of initiation of the reactions. R. T.

Preparation of ethylbenzene from naphthalene.—See B., 1941, II, 209.

***m*-Bromo-*n*-alkylbenzenes.** C. S. Marvel and D. G. Botteron (*J. Amer. Chem. Soc.*, 1941, **63**, 1482—1483).—*m*-$C_6H_4Br{\cdot}CHO$ and MgEtBr give a carbinol, dehydrated (crude) by $KHSO_4$ to *m*-$C_6H_4Br{\cdot}CH_2{\cdot}CH{:}CH_2$ (71%), b.p. 108—114°/16 mm., which with H_2–PtO_2 in EtOH gives *m-bromo-*n*-propylbenzene*, b.p. 96—100°/17 mm. $MgPr^{\alpha}Br$ gives similarly *m*-$C_6H_4Br{\cdot}CH_2{\cdot}CH{:}CHMe$, b.p. 126—130°/22 mm., and *m-bromo-*n*-butylbenzene*, b.p. 113—116°/18 mm. R. S. C.

Synthesis of diaryliodonium salts. R. H. Freidlina and A. N. Nesmejanov (*Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **29**, 567—570).—ICl_3 in dil. HCl yields with $SnPhCl_3$, $PhICl_2$ and Ph_2ICl (82% yield) successively, with $HgPh_2$, Ph_2ICl, $HgCl_2$ (51%, together with some PhI), and with HgPhCl at 100°, Ph_2ICl (42%). A. Lt.

Reaction between lithium and diphenylacetylene. L. I. Smith and H. H. Hoehn (*J. Amer. Chem. Soc.*, 1941, **63**, 1184—1187).—Data of Bergmann *et al.* (A., 1928, 1031; 1931, 948; 1933, 268) have been corr. and extended. $(:CPh)_2$ (1 mol.) and Li (2 atoms) in Et_2O at room temp. give a red salt, $(\cdot CPh{:}CPhLi)_2$, hydrolysed by dry EtOH to $(\cdot CPh{:}CHPh)_2$ (**I**), m.p. 182·5—183°, but, when an excess of Li is used, this salt is later replaced by a sticky brown salt (**II**), hydrolysed to 1 : 2 : 3-$C_{10}H_5Ph_3$ (**III**), m.p. 151°. With S at 250°, (**I**) gives tetraphenylthiophen, white, m.p. 184°, with Na–$C_5H_{11}{\cdot}OH$ gives $(\cdot CHPh{\cdot}CH_2Ph)_2$, m.p. 179—180° (lit. 178°), and with Br–Et_2O at room temp. gives 1 : 2-diphenyl-3-benzylideneindene, yellow, m.p. 184° (cf. Orechoff, A., 1914, i, 266). Carbonation of (**II**) gives a *substance*, $C_{29}H_{20}O_2$, softens at 261°, m.p. 265° (decomp.), insol. in alkali (cf. Bergmann, *loc. cit.*). Bromination of (**III**) failed, but HNO_3 and a drop of H_2SO_4 in AcOH at 90° give a NO_2-derivative, m.p. 200—201°; with Zn in aq. AcOH this gives a mixture, m.p. 189—190°, and no amine could be prepared. R. S. C.

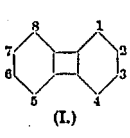
Hexabenzylethane. G. A. Hill, W. C. Nelson, R. L. Dunnell, and L. S. Moody (*J. Amer. Chem. Soc.*, 1941, **63**, 1367—1368).—*ββ′β″-Triphenyl-*tert.*-butyl bromide* (prep. from the carbinol by boiling PBr_3), m.p. 158°, and Zn dust in C_6H_6 at 50° give 5·5% of *hexabenzylethane* [*αδ-diphenyl-ββγγ-tetrabenzyl-*n*-butane*], m.p. 195°, b.p. 209°/5 mm. [$(NO_2)_6$-derivative, m.p. 174—179°]. Other metals and conditions are less satisfactory. In all cases $CHPh{:}C(CH_2Ph)_2$ (up to 90%), m.p. 33·8°, is also formed. R. S. C.

Decahydronaphthalene series. I. Synthesis of β-substituted *cis*- and *trans*-decahydronaphthalenes with saturated or unsaturated side-chains consisting of three carbon atoms. R. J. Levina and S. G. Kulikov (*J. Gen. Chem. Russ.*, 1940, **10**, 1189—1198).—$CH_2{:}CH{\cdot}CH_2Cl$ and 2-chloro-*cis*- or *-trans*-decahydronaphthalene yield, by the Grignard reaction, 2-*allyl*-cis-, b.p. 109°/12 mm., or -trans-*decahydronaphthalene*, b.p. 105°/12 mm., which with Br in Et_2O give the corresponding *βγ-dibromopropyl* derivatives, b.p. 181—183°/9 mm. and 171—173°/9 mm., respectively, and these react with $NaNH_2$ to furnish 2-Δ^{β}-*propinyl*-cis-, b.p. 124—125°/12 mm., and -trans-*decahydronaphthalene*, b.p. 116°/12 mm.; the corresponding 2-*Pr* compounds, b.p. 106°/12 mm. and 102°/12 mm., respectively, were prepared by hydrogenation of the allyl derivatives. By-products of the Grignard reactions are *ββ*-di-*cis*-, m.p. 167—168°, and *-trans*-decahydronaphthyl, m.p. 106—107°, not previously prepared in the cryst. form. R. T.

Synthesis of 10-*cyclo*hexyl-2-methylanthracene. A. T. Martschevski and M. I. Uschakov (*J. Gen. Chem. Russ.*, 1940, **10**, 1369—1372).—*o*-Carboxyphenyl *p*-tolyl ketone and excess of Mg *cyclo*hexyl bromide in Et_2O at 0° yield 1-*keto*-2-cyclo*hexyl*-2-p-*tolyl*iso*benzfuran*, m.p. 113·5—115°, converted by Zn–Hg in AcOH–HCl (15 hr. at the b.p.) into cyclo*hexyl*-2-*carboxy*-2′-*methyldiphenylmethane*, m.p. 155—156°, condensed by heating for 20 min. at 180—190° to 10-cyclo*hexyl*-2-*methyl*-9-*anthrone*, m.p. 112—113·5°. This is reduced with Zn in aq. NH_3 (6 hr. at the b.p.) to 9-*hydroxy*-10-cyclo*hexyl*-2-*methyl*-9 : 10-*dihydroanthracene*, m.p. 166—167·5°, dehydrated by Ac_2O (3—4 min. at the b.p.) to 10-cyclo*hexyl*-2-*methylanthracene*, m.p. 116·5—117°. R. T.

Dehydration of 9-fluorenylcarbinol. Synthesis of phenanthrene. W. G. Brown and B. Bluestein (*J. Amer. Chem. Soc.*, 1940, **62**, 3256—3257).—9-Formylfluorene is reduced by $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$–Et_2O at 60—70° to 9-*fluorenylcarbinol*, m.p. 99·5—100° (3 : 5-*dinitrobenzoate*, m.p. 212°), which with P_2O_5 in boiling xylene gives phenanthrene in almost quant. yield. R. S. C.

Diphenylene. W. C. Lothrop (*J. Amer. Chem. Soc.*, 1941, **63**, 1187—1191).—Distillation of $(o\text{-}C_6H_4Br)_2$ with Cu_2O gives 5% of *diphenylene* (I), yellow, m.p. 110° (scarlet *picrate*, m.p. 122°), but CaO, Al_2O_3, ZnO, CuO, and pure Cu are without effect, and hot H_2–Cu or Li, Na, or K gives Ph_2. A better yield of (I) is obtained by heating diphenyliodonium iodide (Mascarelli, A., 1909, i, 94) with Cu_2O, much *o*-C_6H_4PhI and a little carbazole, phenazone, and a substance (picrate, m.p. 175—178°) being also obtained. CrO_3 oxidises (I) to *o*-$C_6H_4(CO_2H)_2$. Passage of (I) in H_2 over red-hot Cu gives Ph_2 (30%). (2 : 4 : 1-$NH_2{\cdot}C_6H_3Me)_2$ gives (4 : 2-$C_6H_3MeBr)_2$, m.p. 74—75° (lit. 114—115°) (structure proved by oxidation by boiling aq. HNO_3 to 2 : 2′-dibromodiphenyl-4 : 4′-dicarboxylic acid), which with Cu_2O gives 2 : 7-*dimethyldiphenylene* (II), yellow, m.p. 112° (*picrate*, +2EtOH, m.p. 110—111°), better (4·5%) obtained from 2 : 7-dimethyldiphenyliodonium iodide, m.p. 200—202° (decomp.). (2 : 5 : 1-$NH_2{\cdot}C_6H_3Me)_2$ (prep. described), m.p. 78—79°, gives 3 : 6-*dimethyldiphenyleneiodonium iodide* (25%), m.p. 230° (decomp.) [and a little (5 : 2 : 1-$C_6H_3MeI)_2$ (III), m.p. 172°], which with Cu_2O yields (II) and some (III). This is regarded as proof of the structure of (I) and (II). R. S. C.



(I.)

Production of water-soluble high-molecular α-substituted aralkylamines and derivatives thereof.—See B., 1941, II, 252.

Manufacture of substituted arylamines.—See B., 1941, II, 251.

Derivatives of *o*-1-naphthoylbenzoic acid and 1-benzylnaphthalene-2′-carboxylic acid. G. M. Badger (*J.C.S.*, 1941, 351—352).—Et *o*-1-naphthoylbenzoate, new m.p. 81·5—83°, and N_2H_4,H_2O–EtOH at 120° yield 4-*keto*-1-(1′-*naphthyl*)-3 : 4-*dihydrophthalazine*, m.p. 252—253°. Et 1-benzylnaphthalene-2′-carboxylate similarly gives o-1-*naphthylmethylbenzhydrazide*, m.p. 175—176°, converted through the azide into the corresponding *urethane*, m.p. 113—114°, which is hydrolysed by conc. aq. NH_3 at 180° to 1-o-*aminobenzylnaphthalene*, m.p. 101—102°. A. T. P.

Substitution in polycyclic systems. II. Nitro-derivatives of 9-fluoryltrimethylammonium compounds. S. V. Anantakrishnan and V. Pasupati (*Proc. Indian Acad. Sci.*, 1941, **13, A**, 211—220).—Reduction of fluorenoneoxime appears to give a single 9-aminofluorene, readily transformed by NaOH–Me_2SO_4 into 9-fluoryldimethylamine (I), m.p. 49—50° (picrate, m.p. 203—204°). 9-Bromofluorene and an excess of NMe_3 in MeCN at 0° afford 9-fluoryltrimethylammonium bromide (II), m.p. 189—190° [corresponding *picrate* (III), m.p. 170—175°, also obtained from (I)]. Nitration of (II) invariably gives compounds with nuclear Br and it is therefore converted by $AgNO_3$ into the corresponding nitrate, m.p. 194°, which with conc. HNO_3 in Ac_2O at $<-10°$ gives 2-nitro-9-fluoryltrimethylammonium nitrate, characterised as the *picrate*, m.p. 225—226°; the corresponding *bromide*, m.p. 198—200°, is obtained from 9-bromo-2-nitrofluorene. (III) is transformed by drastic treatment with a large excess of fuming HNO_3 into the 2 : 7-$(NO_2)_2$-compound, m.p. 236° (also obtained from 9-bromo-2 : 7-dinitrofluorene through the corresponding quaternary *bromide*, m.p. 225°). 2 : 5-Dinitro-9-fluoryltrimethylammonium picrate has m.p. 209—210°. The 9-substituent does not appear to have any marked influence on the position of the new entrant groups but exerts a noticeable effect on the activity of the nuclear positions. The converse influence of nuclear substituents on the activity of the 9-position is evident. H. W.

Substituted sulphanilamides.—See B., 1941, III, 216.

4-Aminodiphenyl-4′-sulphonamide and derivatives. II. C. T. van Meter and A. Lowy (*J. Amer. Chem. Soc.*, 1941, **63**, 1330—1331; cf. A., 1941, II, 220).—Addition of NH_2R–$COMe_2$ to *p*-NHAc·$C_6H_4{\cdot}C_6H_4{\cdot}SO_2Cl$-*p* and a little C_5H_5N in $COMe_2$ at 50° and keeping the mixture at room temp., followed by hydrolysis by conc. HCl–EtOH, gives 4-*aminodiphenyl-4′-sulphon-anilide*, m.p. 186° (4-*Ac* derivative, m.p. 237°), *-benzylamide*, m.p. 184° (4-*Ac* derivative, m.p. 208°), -cyclo*hexylamide*, m.p. 219° (4-*Ac* derivative, m.p. 244°), and -p-*xenylamide*, m.p. 216° (4-*Ac* derivative, m.p. 250°), N¹-4-*aminodiphenyl-4′-sulphonsulphanilamide*, m.p. 252° (decomp.) (4-*Ac* derivative, m.p. 274°), and 4-4‴-*aminodiphenyl-4″-sulphonamidodiphenyl-4′-sulphonamide*, m.p. 277° (decomp.) (4‴-*Ac* derivative, m.p. 299°). R. S. C.

Optically active [azo-]dyes. Molecular asymmetry in dyes and their dyeing properties.—See B., 1941, II, 256.

Dyes with asymmetric molecules. A. Korolev and I. Bilik (*Compt. rend. Acad. Sci. U.R.S.S.*, 1940, **29**, 586—588).—*d*- and *l*-Forms, $[\alpha]_D^{20}$ ±3000—10,000° (initial), 31,500° (final) (rate of mutarotation depending on p_H, temp., and presence of electrolytes), of the dye (Na_2 salt) prepared by coupling diazotised *d*- and *l*-6′-nitro-6-amino-2 : 2′-dimethyldiphenyl (I), m.p. 122—123°, $[\alpha]_D^{20}$ ±62°, with 5 : 5′-dihydroxy-2 : 2′-dinaphthylcarbamide-7 : 7′-disulphonic acid (II) are adsorbed at the same rate by silk, wool, or vegetable fibre. Dyes from diazotised (I) and 1 : 8 : 3 : 6-$NH_2{\cdot}C_{10}H_4(OH)(SO_3H)_2$ or 2 : 5 : 7-$NH_2{\cdot}C_{10}H_5(OH){\cdot}SO_3H$, and from diazotized *d*-aminomandelic acid and (II), have considerably smaller $[\alpha]_D$. A. Li.

Compound of xenon with phenol.—See A., 1941, I, 342.

Rate studies in the electrochemical oxidation of phenol.—See A., 1941, I, 342.

Effect of a mixture of alcoholic solutions of iodine and silver nitrate on phenols. J. A. Fialkov and A. I. Gengrinovitsch (*Ber. Inst. Chem. Akad. Wiss. Ukrain.*, 1940, **7**, 125—140).—Phenols are iodinated by mixing 100 c.c. of each of 2% I and 2% $AgNO_3$ in EtOH, immediately adding 100 c.c. of a 0·01M-phenol solution in H_2O or EtOH, shaking, and 15 min. later adding 50—100 c.c. of 10% aq. KI. The ppt. is a mixture of AgI and $AgIO_3$, and the liquid (*A*) contains the iodinated phenol. Aq. solutions of I and $AgNO_3$ are inactive, and EtOH solutions of I alone iodinate very little. The iodinating agent is presumably INO_3 or HOI. Titration of (*A*) with $Na_2S_2O_3$ shows that PhOH, resorcinol, *m*-cresol, and salicylic acid consume 6, *β*-$C_{10}H_7{\cdot}OH$ 4, and Zn sulphophenoxide 8 I. J. J. B.

m-**Diphenylyl acetate.** S. E. Hazlet and H. A. Kornberg (*J. Amer. Chem. Soc.*, 1941, **63**, 1482).—This *substance* has m.p. 34·0—34·2° (corr.), b.p. 135—136°/2 mm. R. S. C.

Triaryl phosphates.—See B., 1941, II, 253.

Reaction between diphenylketen and arylacetylenes. II. *p*-**Tolylacetylene. III.** *α*-**Diphenylacetyl-**β**-phenylacetylene. IV. Synthesis of 1 : 4-diphenyl-**β**-naphthol. V. Diphenylacetylene. VI. Mechanism.** L. I. Smith and H. H. Hoehn (*J. Amer. Chem. Soc.*, 1941, **63**, 1175—1176, 1176—1178, 1178—1179, 1180—1181, 1181—1184).—II. In the formation of 3 : 4-diaryl-*α*-naphthols from $CPh_2{:}CO$ (I) and $CH{:}CAr'$ (A., 1939, II, 543), the Ar′ enters the 3-position. *p*-$C_6H_4Me{\cdot}CCl{:}CH_2$ (prep. in 68·5% yield from *p*-$C_6H_4Me{\cdot}COMe$ by PCl_5, first at <0° and then at room temp.), b.p. 81—83°/10 mm., and boiling 1 : 2 KOH–EtOH give *p*-$C_6H_4Me{\cdot}C{:}CH$ (65%), b.p. 79—82°/31—33 mm., which with (I) in N_2 at room temp. gives 4-*phenyl*-3-*p*-*tolyl*-*α*-*naphthol* (77%), m.p. 153—154° {*acetate*, m.p. 131—132°; 1 : 2-*quinone* [prep. by $Pb(OAc)_4$–AcOH], m.p. 226—227° (*phenazine* derivative, m.p. 283—284°)}, oxidised by boiling $KMnO_4$–KOH to *o*-$C_6H_4Bz{\cdot}CO_2H$ and *p*-$C_6H_4(CO_2H)_2$.

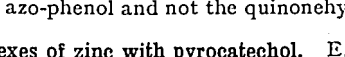
III. $CPh{:}C{\cdot}MgBr$ and (I) in boiling Et_2O give a good yield of *aδδ-triphenyl-*Δ^{α}*-butinen-γ-one* (II), m.p. 97—98° (*semicarbazone*, m.p. 197—198°), hydrogenated (PtO_2; AcOH; 35 lb.) to *aaδ-triphenylbutan-*β*-one* (III), m.p. 62°, also obtained as follows. Et lactate and MgPhBr in Et_2O give $OH{\cdot}CHMe{\cdot}CPh_2{\cdot}OH$, m.p. 95°, converted by a trace of HCl in H_2O at 180° into $CHPh_2{\cdot}COMe$; with PhCHO and NaOH in EtOH at room temp. this gives $CHPh{:}CH{\cdot}CO{\cdot}CHPh_2$ and thence (H_2–PtO_2; EtOH) (III). (II) and (III) slowly decompose to oils when kept. $ZnCl_2$ in boiling AcOH has no effect on (II), which is thus not an intermediate in the reaction of $CH{:}CPh$ with (I).

IV. 2-Hydroxy-1 : 4-naphthaquinone (modified prep.) and boiling HCl–MeOH give the 2-OMe-quinone, m.p. 181—183°, which by double 1 : 2 addition of MgPhBr in boiling Et_2O gives 1-*hydroxy*-2-*keto*-1 : 4-*diphenyl*-1 : 2-*dihydronaphthalene* (IV), m.p. (+AcOH) 103° and (solvent-free) 122° [*oxime*, m.p. 193—194° (decomp.)]. Zn dust in AcOH reduces (IV) to 1 : 4-*diphenyl-*β*-naphthol*, m.p. 117—118° {negative $FeCl_3$, positive Folin test; *acetate*, m.p. 157°; oxidised by CrO_3–AcOH to *o*-$C_6H_4Bz_2$ [also obtained by oxidation of (IV)]}, and differing from the *α*-naphthol yielded by $CH{:}CPh$ and (I).

V. $(CPh{:})_2$ [prep. from $(:CHPh)_2$ by way of the dibromide described], m.p. 60—61°, and (I) (excess) in CO_2 at 70—80° give after 3 days 2 : 3 : 4-*triphenyl-α-naphthyl diphenylacetate* (V), m.p. 168—169°, hydrolysed by KOH–aq. MeOH to 2 : 3 : 4-*triphenyl-α-naphthol* (VI), m.p. 163° (*acetate*, m.p. 194°; oxidised to *o*-$C_6H_4Bz{\cdot}CO_2H$). Condensation of a 1 : 1 (mol.) mixture for 1 day gives a yellow phenolic mixture of (V) and, probably, (VI).

VI. Condensation of $CH{:}CPh$ and (I) proceeds by way of 2 : 2 : 3-triphenyl-Δ^3-*cyclo*butenone and thence one of three possible substances, the route by way of a Diels–Alder condensation being rejected on facts collated from the literature. However, attempted proofs of the hypothesis failed. 2 : 2 : 3-Triphenyl*cyclo*butanone resists dehydrogenation by chloranil in boiling PhMe, and hydrogenation (PtO_2) of the viscous products from $CH{:}CPh$ and (I) in EtOH at 35 lb. gives only 3 : 4 : 1-$C_{10}H_5Ph_2{\cdot}OH$. R. S. C.

Inner complexes of benzeneazo-phenanthrol, -retenol, and -chrysenol. H. M. Haendler and G. McP. Smith (*J. Amer. Chem. Soc.*, 1941, **63**, 1371—1372).—Absorption spectra of 9-benzeneazo-10-phenanthrol, m.p. 162°, 9-benzeneazo-10-retenol, m.p. 159—160·5°, and 5-*benzeneazo*-6-*chrysenol*, m.p. 219—220° (prepared from the quinones by $NHPh{\cdot}NH_2$), and their *Cu* derivatives (absorption similar with much higher ϵ) resemble those of the naphthol series. The compounds thus have the azo-phenol and not the quinonehydrazone structure. R. S. C.

Complexes of zinc with pyrocatechol. E. Sellés (*Anal. Fis. Quim.*, 1941, **37**, 114—115).—The following have been prepared:  , where R_2 is Na_2, $(NH_4)_2,2H_2O$, or K_2. F. R. G.

Preparation of hydroxyquinol.—See B., 1941, II, 253.

Condensation of diketones with phenol. J. B. Niederl and R. H. Nagel (*J. Amer. Chem. Soc.*, 1941, **63**, 1235—1237).—PhOH, $(CH_2Ac)_2$, and HCl, first at room temp. and then in boiling AcOH, give *ββεε-tetra*-p-*hydroxyphenyl*-n-*hexane*, m.p. 298° [*tetra-acetate*, m.p. 186°; *tetrapropionate*, m.p. 116—118°; $(NO_2)_8$-derivative, decomp. 300—305°; $(Hg{\cdot}OAc)_8$ derivative, decomp. 320—340°]. Bz_2, PhOH, and HCl in AcOH at room temp. give *benzoylphenyldi*-p-*hydroxyphenylmethane* (I), m.p. 212° (*diacetate*, m.p. 168°; *dipropionate*, m.p. 123—125°), by way of $(p{\text{-}}OH{\cdot}C_6H_4{\cdot}CPh{\cdot}OH)_2$ and thence the ethylene oxide which undergoes pinacolinic rearrangement. Na–$C_5H_{11}{\cdot}OH$ reduces (I) to *αβ-diphenyl-ββ-di*-p-*hydroxyphenylethyl alcohol*, m.p. 152—154° (*triacetate*, m.p. 114—116°). R. S. C.

Invert soaps. Quaternary ammonium salts of derivatives of long-chain phenols. J. B. Niederl and M. I. Dexter (*J. Amer. Chem. Soc.*, 1941, **63**, 1475—1476).—*p*-*p*-$OMe{\cdot}C_6H_4{\cdot}CMe_2{\cdot}CH_2Bu^{\gamma}$, m.p. 46°, b.p. 272°, and conc. HNO_3 in 1 : 1 AcOH–Ac_2O at +10°, later room temp., give the 2-NO_2-derivative, m.p. 58°, b.p. 151°/3 mm., reduced by Sn–conc. HCl–EtOH to 2-*amino*-, b.p. 160°/8 mm. (*hydrochloride*, m.p. 75—77°; *Bz* derivative, m.p. 111°), which with Me_2SO_4 at 100° gives 2-*dimethylamino*-4-*aayy-tetramethyl*-n-*butylanisole*, b.p. 163—165°/8 mm. (*methiodide*, m.p. 172°; *methosulphate*, m.p. 154°). R. S. C.

Hydrolysis of β**-naphthol-8-sulphonic acid during sulphonation of** β**-naphthol.**—See B., 1941, II, 245.

β**-Tolyl***iso***propyl alcohols.** J. G. Sharefkin and J. J. Ritter (*J. Amer. Chem. Soc.*, 1941, **63**, 1478—1479).—*p*- or *m*-$C_6H_4Me{\cdot}MgBr$ and propylene oxide in Et_2O and then Et_2O–C_6H_6 give *β-p-*, b.p. 84—85°/2 mm. [*phenylurethane*, m.p. 110—111·5°; some $(p{\text{-}}C_6H_4Me)_2$ is also formed], and *β-m*-tolyl-*iso*propyl alcohol, b. p. 89—91°/2 mm. (*phenylurethane*, m.p. 77·5—78°). R. S. C.

1-Phenyl*cyclo***heptanol.** R. D. Kleene (*J. Amer. Chem. Soc.*, 1941, **63**, 1482).—*cyclo*Heptanone and MgPhBr in Et_2O give 1-*phenyl*cyclo*heptanol*, an oil. R. S. C.

Periodic law. P. I. Petrenko-Kritschenko (*J. Gen. Chem. Russ.*, 1940, **10**, 1305).—Change in colour of $CHPh_3$ dyes with increase in the no. of identical substituents takes place according to a periodic rule. Hantzsch's quinonoid theory is criticised. R. T.

Transformation of cholesterol by the action of ultra-violet light in contact with air. S. A. Neufach (*Biochimia*, 1940, **5**, 348—357).—Cholesterol (I) in contact with air irradiated with ultra-violet light gives a product which differs from (I) in its diminished solubility in Et_2O, and increased solubility in EtOH and $COMe_2$, its reduced m.p., its lower sp. rotation, its absorption spectrum, and its blue-violet fluorescence (spectrum identical with that of ergosterol) in $COMe_2$. A. L.

Photometric determination of the rapidity of ergosterol transformation on irradiation with ultra-violet light. E. A. Markarian (*Biochimia*, 1940, **5**, 321—330).—The photochemical transformation products of ergosterol (I) have no effect on the determination of (I) in irradiated samples by a modification of the nephelometric method of Mühlbock *et al.* (A., 1932, 666). The method can therefore be used to determine the rapidity of photochemical transformation. A. L.

Steryl sulphates. I. Preparation and properties. A. E. Sobel and P. E. Spoerri (*J. Amer. Chem. Soc.*, 1941, **63**, 1259—1261).—Cholesterol with C_5H_5N,SO_3 and a little C_5H_5N–Ac_2O in C_6H_6 quantitatively or, for a purer product, with a deficiency of C_5H_5N–SO_3 in C_6H_6 at 56—60° gives *cholesteryl* C_5H_5N *sulphate*, m.p. 179°, $[\alpha]_D^{26}$ −23·8° in $CHCl_3$, sol. (10—15%) in H_2O, stable in strong acid at room temp. and in boiling strong alkali. Double decomp. then gives *cholesteryl K*, $+H_2O$, m.p. 210° or decomp. 239°, *Na*, $+6H_2O$, m.p. 177—178·5°, *Ca*, m.p. variable, ~136°, *Ba*, $+3H_2O$, m.p. 124°, *Mg*, $+6H_2O$, m.p. 152—154°, *Ag*, red at 117°, m.p. 124°, *Pb*, m.p. 132—134°, *Hg·OAc*, m.p. 152—171°, and Cu (very unstable), m.p. 150°, *sulphate*. Similarly are prepared *ergosteryl* C_5H_5N, m.p. 194—196°, *K*, $+H_2O$, m.p. 211°, *Na*, $+3H_2O$, m.p. 164—166°, *Ca*, $+5H_2O$, m.p. 135°, *Mg*, $+8H_2O$, m.p. 145—148°, and Ba (unstable) *sulphate*, m.p. 145°, *lanosteryl* C_5H_5N, m.p. 160—168°, and *K sulphate*, m.p. 199—200° (other salts sol.), *dibromodihydrocholesteryl* C_5H_5N, m.p. 135°, *Na*, *K*, *Ca* (+1·5$CaSO_4$), and Hg (+1·5HgO), m.p. 123°, *sulphate*. M.p. are with decomp. R. S. C.

Conversion of 6-chloro-3-benzoyloxy-Δ^4-cholestene into $\Delta^{4:6}$-cholestadienyl benzoate. F. S. Spring and G. Swain (*J.C.S.*, 1941, 320—323; cf. A., 1939, II, 477).—6-Chloro-3-benzoyloxy-Δ^4-cholestene and $AgNO_3$–C_5H_5N at room temp. give a pyridinium *salt* (**I**), m.p. 158—159°, and the monobenzoate (**II**), m.p. 153—154°, of *cis*-3 : 4-dihydroxy-Δ^5-cholestene; at 90°, (**I**), (**II**), and $\Delta^{4:6}$-*cholestadienyl benzoate* (**III**), m.p. 128—129°, $[\alpha]_D^{21}$ −81° in $CHCl_3$, result. Cholesterol dibromide and $AgNO_3$–C_5H_5N at room temp. for 5 days (in the dark) yield (chromatographic separation) Δ^4-cholestenone (mechanism of formation discussed), 3 : 6-diketo-Δ^4-cholestene, m.p. 121—122°, and a fraction, m.p. 119—120°, $[\alpha]_D^{20}$ −27·4° in $CHCl_3$, containing much $\Delta^{4:6}$-cholestadienol (**IV**), since benzoylation gives (**III**) and acetylation affords $\Delta^{4:6}$-cholestadienyl acetate (**V**), m.p. 77—78°, $[\alpha]_D^{20}$ −67° in $CHCl_3$. The esters of (**IV**) are stable and are characterised by a single intense absorption max. at 2390 A.; (**IV**) is not stable to alkali. Hydrolysis of (**V**) with KOH–EtOH–MeOH at 20° for 70 hr. affords a product, m.p. 116—117°, $[\alpha]_D^{18}$ −34·9° in $CHCl_3$, whilst (**III**) and boiling KOH–MeOH give a product, m.p. 124—125° (cf. Dane *et al.*, A., 1937, II, 417; Petrow, A., 1940, II, 84). A. T. P.

Sterol group. XLIII. Unsaponifiable portion of the acetone extract of plantation rubber. I. M. Heilbron, E. R. H. Jones, K. C. Roberts, and P. A. Wilkinson (*J.C.S.*, 1941, 344—347). —The sterol (*A*), composition $C_{29}H_{50}O$ (+0·5EtOH), m.p. 133·5° (cf. Whitby *et al.*, A., 1926, 841) [H_2-derivative, m.p. 134·5—135·5°; acetate, m.p. 123·5° (H_2-derivative, m.p. 130·5°); benzoate, m.p. 147·5°; *p*-nitrobenzoate, m.p. 183—184°], from the $COMe_2$ extract of crêpe rubber, with Se at 320—400° affords a *chrysene*, $C_{21}H_{18}$, m.p. 172—173°, a *picene*, $C_{25}H_{20}$, m.p. 274—276°, and a *hydrocarbon*, $C_{25}H_{24}$, m.p. 227° (2 : 7-*dinitroanthraquinone* derivative, m.p. 242—243°) (cf. Ruzicka *et al.*, A., 1934, 398). Chromatographic analysis, although not allowing the isolation of a pure compound, showed (*A*) to be a mixture. Fractional crystallisation of the acetate of (*A*) affords β-sitosteryl acetate and the acetate (**I**), m.p. 114—116° [H_2-derivative (**II**), m.p. 122—123°], of a sterol (**III**) (composed mainly of 24 : 28-dehydrostigmastanol), m.p. 134° (H_2-derivative, m.p. 126·5—127°; benzoate, m.p. 145°). Ozonolysis of (**I**) gives MeCHO, but (**II**) similarly affords only a trace of CH_2O. $Al(OBu^{\gamma})_3$–$COMe_2$ and (**III**) give a ketone, m.p. 92—95°. The red gum, obtained from the alcoholic mother-liquor from the crude sterol, when distilled at 10^{-3} mm., affords eicosyl alcohol, m.p. 62° (*phenylurethane*, m.p. 75—76°) (not octadecyl alcohol as stated by Bruson *et al.*, B., 1927, 884), and a steroid ketone (2 : 4-*dinitrophenylhydrazone*, $C_{35}H_{52}O_4N_4$, m.p. 239—240°); extensive pyrolysis occurs also. A. T. P.

Esters of 7-hydroxycholesterol.—See B., 1941, III, 217.

Metabolism of steroids. II. Isolation of cholestane-3 : 5 : 6-triol and other substances from ox liver extracts. G. A. D. Haslewood (*Biochem. J.*, 1941, **35**, 708—711).—α-7-Hydroxycholesterol, m.p. 174—176° (decomp.), cholestane-3 : 5 : 6-triol, m.p. 235—237°, and a non-steroid *alcohol*, ? $C_{24}H_{46}O_3$, m.p. 93—95° (*acetate*, m.p. 103—105°, 107—108°), have been isolated from the non-saponifiable fraction of an Et_2O extract of ox liver. The previously described "hepatol *A*" (A., 1939, III, 707) is digitogenin; oxidation of its diacetate with AcOH–CrO_3 at room temp. yields an *acid*, $C_{30}H_{45}O_7{\cdot}CO_2H$, m.p. 263—264° (decomp.) (*Me* ester, m.p. 184—186°). P. G. M.

Constituents of the adrenal cortex and related substances. XLVI. Transformation of substance *K* into substances *J* and *O*. D. A. Prins and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 396—400).—Substance *K* is oxidised by HIO_4 in aq. dioxan to 17-*formylandrostane*-3(β) : 17(β)-*diol* (probably semihydrate), m.p. 150—153°, $[\alpha]_D^{17}$ −16·6°±3° in EtOH, which (crude form) is transformed by MgMeBr followed by acetylation into substance *J* diacetate, $[\alpha]_D^{15}$ +24·3°±4° in $COMe_2$, and substance *O* diacetate, $[\alpha]_D^{15}$ −32·9°±4°, $[\alpha]_{5461}^{15}$ −39·4°±4° in $COMe_2$. Δ^4-Pregnene-17(β) : 20(β) : 21-triol-3-one is similarly oxidised to Δ^4-17-*formylandrosten*-17(β)-*ol*-3-*one*, m.p. 142—146°, $[\alpha]_D^{15}$ +49·4°±3° in $COMe_2$ (*semicarbazone*, m.p. >350° after much darkening at 280—300°). H. W.

Chaulmoogric acid series. III. Synthesis of *dl*-hydnocarpic acid. K. V. Bokil and K. S. Nargund (*Proc. Indian Acad. Sci.*, 1941, **13, A**, 233—239).—Et κ-1-carbethoxy-2-keto*cyclo*pentylundecoate (cf. A., 1938, II, 186) is not appreciably reduced by a large excess of Na–Hg in aq. EtOH but is converted by KOH–EtOH (containing KOEt) into *n-tetradecane-*αδζ*-tricarboxylic acid*, m.p. 92—93° (*K* H_2 salt). This is not conveniently esterified by the Fischer–Speier process but is transformed through the Ag_3 salt into the Et_3 ester, b.p. 250—260°/5 mm. (some decomp.). This is cyclised (Na in boiling C_6H_6) to Et κ-3-carbethoxy-2-keto*cyclo*pentylundecoate (*semicarbazone*, m.p. 146—147°, becoming clear at 150°), which could not be distilled without decomp. under greatly reduced pressure but is reduced to the non-purifiable OH-ester. This is hydrolysed to the dibasic OH-acid, which is dehydrated (boiling Ac_2O) to *dl*-hydnocarpic acid, m.p. 58—59° (amide, m.p. 109—110°), and κ-3-*carboxy*-Δ^2-cyclo*pentenylundecoic acid*, m.p. 82—83° (sinters at 79°), separated from one another through the Ba salts. H. W.

4-Methoxy*cyclo*hexylacetic acid. P. Ruggli, O. Leupin, and A. Businger (*Helv. Chim. Acta*, 1941, **24**, 339—346).—The main product of the hydrogenation of *p*-OMe·C_6H_4·CH_2·CO_2H in presence of PtO_2 is *cyclo*hexylacetic acid, OMe being lost as MeOH and the double linking thus formed being hydrogenated. Conversion of *p*-OMe·C_6H_4·OH into 4-methoxy*cyclo*hexanol (**I**), b.p. 98—99°/11 mm., is best effected under pressure in presence of the Rupe or Raney catalyst (95% yield); PtO_2 causes marked demethylation and gives only a 30% yield. Transformation of (**I**) into the halide and treatment of the latter with $CHNa(CO_2Et)_2$ causes much elimination of HHal with formation of the *cyclo*hexene derivative. (**I**) is therefore converted by successive treatments with Na powder and *p*-$C_6H_4Me{\cdot}SO_2Cl$ in C_6H_6 into 4-*methoxy*cyclo*hexyl* p-*toluenesulphonate*, m.p. 86—87° (accompanied by a stereoisomeride), which with $CHNa(CO_2Et)_2$ in boiling EtOH gives *Et*$_2$ 4-*methoxy*cyclo*hexylmalonate* (**II**), b.p. 165—170°/12 mm., hydrolysed and decarboxylated to 4-*methoxy*cyclo*hexylacetic acid*, solid (? *trans*), m.p. 77—78°, and (mainly) liquid form (**III**). $SOCl_2$ and (**III**) afford the chloride, b.p. 112—118°/12 mm., whence the p-*toluidide*, m.p. 110—113°. (**II**), NaOEt, and $CO(NH_2)_2$ in boiling EtOH give 5-4′-*methoxy*cyclo*hexylbarbituric acid*, m.p. 214—216°, (**II**), NaOEt, and EtI afford Et_2 4-methoxy*cyclo*hexylethylmalonate, b.p. 173—177°/12 mm., whence 5-4′-*methoxy*cyclo*hexyl*-5-*ethylbarbituric acid*, m.p. 239—240°. H. W.

α-4-Methoxy*cyclo*hexylbutyric acid. P. Ruggli and A. Businger (*Helv. Chim. Acta*, 1941, **24**, 346—350).—*Et*$_2$ 4-*methoxy*cyclo*hexylethylmalonate* (cf. preceding abstract) is most conveniently prepared from $CHEt(CO_2Et)_2$ and cryst. 4-methoxy*cyclo*hexyl *p*-toluenesulphonate (**I**) in xylene. The derived malonate is converted by hydrolysis and decarboxylation into a α-4-*methoxy*cyclo*hexylbutyric acid*, b.p. 140—143°/2 mm. (*Et* ester, b.p. 90—92°/2 mm.), which gives a chloride (**II**) and thence a cryst. p-*toluidide*, m.p. 143° (sinters at 140°), and α-*naphthylamide*, m.p. 162—164°; it is regarded as the *trans*-acid. When distilled in a high vac. (**II**) appears to be changed since it no longer gives cryst. derivatives. If the synthesis is effected with the liquid form of (**I**) the product is a α-4-*methoxy*cyclo*hexylbutyric acid*, b.p. 150—155°/3 mm., which does not afford a cryst. *p*-toluidide or α-naphthylamide and is regarded as the *cis*-form. α-*Ethylbutyr*-α-*naphthylamide*, m.p. 128—129°, is incidentally described. H. W.

Synthesis of 4-hydroxy-3-methoxymandelamide. H. Schwartz and J. L. McCarthy (*Canad. J. Res.*, 1941, **19, B**, 150—152).—Vanillin cyanohydrin (**I**) (prep. *in situ*) with Et_2O–EtOH–HCl at 10°, followed by hydrolysis (H_2O + $CaCO_3$) of the imino-ether hydrochloride, gives *Et* 4-*hydroxy*-3-*methoxymandelate*, m.p. 75—77°, converted by EtOH–NH_3 at 0° into 4-*hydroxy*-3-*methoxymandelamide* (**II**), m.p. 136·5—137·5°. The dibenzoate of (**I**) with boiling AcOH–H_2O–ZnO gives the *dibenzoate* (**III**), m.p. 176·5—177·5°, of (**II**). MgMeI and (**II**) or (**III**) did not afford the expected acetylarylcarbinol. The diacetate of (**I**) and Et_2O–C_6H_6–HCl did not yield the corresponding α-chloroacetamide. H. B.

Preparation of basic esters of substituted acetic acids. K. Miescher and K. Hoffmann [with, in part, L. Panizzon] (*Helv. Chim. Acta*, 1941, **24**, 458—465).—Interaction of $CHPh_2{\cdot}COCl$ and $NEt_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ in PhCl at 120—125° or of $CHPh_2{\cdot}CO_2H$, $NEt_2{\cdot}CH_2{\cdot}CH_2Cl$ (**I**), and K_2CO_3 in warm, dry $COMe_2$ gives β-diethylaminoethyl diphenylacetate hydrochloride ("trasentin") (**II**), m.p. 114°; the free *ester*, b.p. 140—145°/0·01 mm., gives a sparingly sol. picrate, m.p. 144—145·5°, and a hydriodide, m.p. 118—119°. *β-Diethylaminoethyl* cyclo*hexylphenylacetate*, b.p. 137°/0·07 mm. (*hydrochloride*, m.p. 146—147°), is obtained from the acid, (**I**), and K_2CO_3 or

by hydrogenation (PtO_2 in AcOH at 50°) of (**II**); it gives an *ethobromide*, m.p. 149—151°, and *benzylobromide*, m.p. 141—142°. β-Piperidinoethyl, b.p. 180—182°/0·15 mm. (*hydrochloride*, m.p. 166—167°), and *tropine*, b.p. 186°/15 mm. (hydrochloride, m.p. 231—233°), cyclo*hexylphenylacetate* are obtained from the acid chloride and the requisite alcohol. *β-Diethylaminoethyl* 1 : 2 : 3 : 4-*tetrahydrodiphenylacetate hydrochloride*, m.p. 153—154°, is derived from the acid, (**I**), and K_2CO_3 in EtOAc at room temp. Complete hydrogenation of (**II**) (H_2–PtO_2–AcOH at 40—45° under slightly increased pressure) gives *β-diethylaminoethyl dodecahydrodiphenylacetate*, b.p. 163°/0·15 mm. (hydrochloride, m.p. 167—169°; sparingly sol. *thiocyanate*, m.p. 93—95°; freely sol., non-cryst. sulphate), also obtained from the acid chloride. Hydrogenation of $CHPh_2{\cdot}CO_2Et$ in abs. EtOH under pressure at 120—130° in presence of reduced Ni on clay until absorption of H_2 ceases gives pure *Et* cyclo*hexylphenylacetate*, b.p. 167°/12 mm., hydrolysed by alkali to the acid, m.p. 150—151°; the Me ester behaves similarly. The acid is also prepared by hydrogenation (H_2 at 135—140°/20—30 atm., Ni–abs. EtOH) of $OH{\cdot}CPh_2{\cdot}CO_2Me$ followed by hydrolysis. H. W.

Azlaotones. V. Preparation of α-benzamidocinnamic acid azlactones I and II. Use of β-phenylethylamine in the purification of α-amino-β-methoxy- (-hydroxy-)acids. H. E. Carter and W. C. Risser (*J. Biol. Chem.*, 1941, **139**, 255—262).—*dl*-α-Benzamido-β-methoxy-β-phenylpropionic acid *A* (**I**), m.p. 153—154°, new m.p. 166—167°, or *B* (**II**), m.p. 220—222° (A., 1938, II, 279) ($Ph{\cdot}[CH_2]_2{\cdot}NH_2$ *salts*, m.p. 184—188° and 169—171°, respectively), with Ac_2O or BzCl in C_5H_5N yields α-benzamidocinnamic acid azlactone I (**III**), m.p. 164—166°. (**II**) with Ac_2O at 100° gives a mixture of (**III**) with the isomeric *azlactone* II (**IV**), m.p. 146—148°. (**III**) and crude (**IV**) with NaOEt in C_6H_6 yield Et α-benzamidocinnamate I, m.p. 142—146°, and II, hydrolysed to α-benzamidocinnamic acid I, m.p. 223—226°, and II (pure), m.p. 199—200°, respectively, reconverted by Ac_2O into (**III**) and (pure) (**IV**), respectively. (**IV**) with C_5H_5N rapidly gives (**III**) at room temp. *α-Carbobenzyloxyamino-β-methoxy-β-phenylpropionic acids* A and B have m.p. 103—105° and 140—142°, respectively ($Ph{\cdot}[CH_2]_2{\cdot}NH_2$ *salts*, m.p. 132—135° and 80—86°, respectively). The $Ph{\cdot}[CH_2]_2{\cdot}NH_2$ *salts* of *N*-benzoyl-*dl*-threonine, -*allo*threonine, -*O*-methylthreonine, and -*O*-methyl*allo*threonine have m.p. 159—162°, 148—152°, 113—117°, and 126—130°, respectively. $Ph{\cdot}[CH_2]_2{\cdot}NH_2$ may be generally useful in separating diastereoisomerides of the type now studied. A. Lt.

Preparation of *S*-benzylthiolacetic acid. G. G. Stoner and G. Dougherty (*J. Amer. Chem. Soc.*, 1941, **63**, 1481).—$CO_2H{\cdot}CH_2{\cdot}S{\cdot}SO_3H$ (prep. *in situ* from $CH_2Cl{\cdot}CO_2Na$ and $Na_2S_2O_3$, followed by HCl) and $CH_2Ph{\cdot}OH$ in aq. HCl give $CH_2Ph{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, m.p. 60—61°, converted by H_2O_2 into the *sulphoxide*, m.p. 126—127°, which with $KMnO_4$ gives $CH_2Ph{\cdot}SO_2{\cdot}CH_2{\cdot}CO_2H$, m.p. 137° (lit. 139—140°). R. S. C.

Mercapturic acid synthesis in animals. XII. Synthesis of *N*-acetyl-*S*-*p*-bromobenzyl-*l*-cysteine in the rat from *p*-bromobenzyl bromide, *S*-*p*-bromobenzyl-*l*-cysteine, and *S*-*p*-bromobenzylglutathione. J. A. Stekol (*J. Biol. Chem.*, 1941, **138**, 225—229).—*l*-Cysteine hydrochloride with EtOH–p-$C_6H_4Br{\cdot}CH_2Br$ (I) in 3N-NaOH yields S-p-*bromobenzyl*-l-*cysteine*, m.p. 213—214°, $[\alpha]_D^{24}$ +23° in N-NaOH (*Ac* derivative, m.p. 118—119°, $[\alpha]_D^{24}$ −37° in EtOH). *N*-Acetyl-*S*-*p*-bromobenzyl-*dl*-cysteine has m.p. 151—152°. The aq. extract of yeast (previously extracted with $COMe_2$) with (**I**) and NaOH yields S-p-*bromobenzylglutathione*, m.p. 199—201°. M.p. are corr. For physiological aspects see A., 1941, III, 524. A. Lt.

High mol. wt. aliphatic amines and their derivatives. W. I. Harber (*Iowa State Coll. J. Sci.*, 1940, **15**, 13—25).—Stearic acid with NH_3 at 330°/9 hr. followed by fractional distillation gives stearonitrile (**I**), m.p. 41—42°, b.p. 185—187°/4 mm. Lauronitrile, b.p. 130—136°/3 mm., and sebaconitrile (**II**), b.p. 168—170°/3 mm., were prepared similarly. (**II**) and NH_3 (160 lb./sq. in.) with H_2 (500 lb./sq. in.) and Raney Ni in light petroleum at 140° for 30 min. gives decane-ακ-diamine (**III**), m.p. 61—61·5°, which readily absorbs CO_2. The amines are converted (standard methods) into NN′-*di*-n-*dodecyl*-, m.p. 74·5—75°, N′-*phenyl*-N-n-*dodecyl*-, m.p. 69·5—69·8°, and NN′-*di*-n-*octadecyl*-*thiocarbamide* (**IV**), m.p. 95—96°; N′-α-*naphthyl*-N-n-*dodecyl*-, m.p. 127·5—128°, NN′-*di*-n-*octadecyl*- (**V**), m.p. 112—112·5°, N′-α-*naphthyl*-N-n-*octadecyl*-, m.p. 122·5—123°, NN-*di*-n-*octadecyl*-, m.p. 65—65·5°, N′-*phenyl*-NN-*di*-n-*octadecyl*-, m.p. 56—56·5°, and N′-α-*naphthyl*-NN-*di*-n-*octadecyl*-*carbamide*, m.p. 54—55°. (**IV**) with hot EtOH–$AgNO_3$ followed by boiling aq. EtOH–KOH gives (**V**). Equimol. amounts of aromatic or high-mol. aliphatic amines heated with carboxylic acids at temp. sufficiently high (usually 250°) to eliminate the steam formed (cleaner products obtained in N_2) afford the corresponding amides. The following are prepared: *benz*- (**VI**), m.p. 85—85·5°, m-, m.p. 71—71·5°, and o-*tolu*-, m.p. 73·5—74°, *anis*-, m.p. 100—100·5°, o-, m.p. 78—78·5°, and p-*chlorobenz*-, m.p. 94—94·5°, *cinnam*-, m.p. 88·5—89°, *laur*-, m.p. 84·5—85°, *myrist*-, m.p. 87·5—87·8°, *palmit*-, m.p. 90—90·5°, *stear*-, m.p. 94·5—95°, *ole*-, m.p. 70—70·5°, and *elaid*-, m.p. 83·5—84° -n-*octadecylamide*; m-, m.p. 47—47·5°, and o-*tolu*-, m.p. 55—55·5°, *anis*-, m.p. 87·5—88°, o-, m.p. 61—61·5°, and p-*chlorobenz*-, m.p. 77—78°, *cinnam*-, m.p. 73—73·5°, *laur*-, m.p. 77—77·5°, *myrist*-, m.p. 83—83·5°, *palmit*-, m.p. 82—82·5°, *stear*- (**VII**), m.p. 84—84·5°, *ole*-, m.p. 49—51°, and *elaid*-n-*dodecylamide*, m.p. 73·5—74°. Similarly (**III**) (1 mol.) with lauric acid (2 mols.) gives NN′-αω-*decamethylenedilauramide*, m.p. 137—137·5°. n-*Dodecyl*-, m.p. 100—137°, and n-*octadecyl*-*ammonium* p-*toluenesulphonate*, m.p. 93—138°, were prepared from the amines and p-$C_6H_4Me{\cdot}SO_3H$. The amines and RCOCl give (**VI**), (**VII**), *benzenesulphon*-n-*dodecyl*-, m.p. 57·5—58°, and -n-*octadecylamide*, m.p. 77—77·5°, and *benzdi*-n-*octadecylamide* (**VIII**), m.p. 55—56°; $(RCO)_2O$ affords (**VIII**), acet-*n*-dodecylamide, m.p. 53·5—54° (lit. b.p. 212—213°/13 mm.), and *phthal*-n-*dodecyl*- (**IX**), m.p. 64—64·5°, and -n-*octadecyl*-*imide* (**X**), m.p. 79—79·5°; the appropriate ester affords NN′-*di*-n-*octadecyl*-*oxamide*, m.p. 119—119·5°, and -*malonamide*, m.p. 126—126·2°. (**IX**) and (**X**) when heated with 10% NaOH for 1 hr. gave n-*dodecyl*-, m.p. 87—88·5°, and n-*octadecyl*-*phthalamic acid*, m.p. 90·5—92·5°, respectively. n-*Dodecylammonium* n-*dodecylcarbamate*, m.p. 85·5—86·5°, and *n*-dodecylaminc hydrochloride, m.p. 181° [lit. 100° (decomp.)], are described. J. L. D.

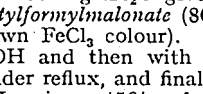
Promoter effect of platinic chloride on Raney nickel. III. Hydrogenation of the nitrobenzoic acids and the nitrobenzene–aniline intermediates. S. S. Scholnik, J. R. Reasenberg, E. Lieber, and G. B. L. Smith (*J. Amer. Chem. Soc.*, 1941, **63**, 1192—1193; cf. A., 1939, I, 208).—H_2PtCl_6 enhances the rate of hydrogenation of *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2Na$ and the corresponding Me and Et esters in 95% EtOH in presence of Raney Ni. NaOH inhibits hydrogenation of the salts but increases that of the esters. Hydrogenation of *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2Na$ ceases after two thirds reduction, probably owing to development of alkalinity since addition of AcOH or hydrogenation in presence of NH_4Cl overcomes this. Hydrogenation (Raney Ni) of $(NPh)_2$, $(NHPh)_2$, and $NHPh{\cdot}OH$ is slower than that of $PhNO_2$, and PhNO poisons Raney Ni (but not PtO_2); these substances are, therefore, not intermediates. R. S. C.

Colour test for *p*-aminobenzoic acid, the chromotrichia factor. H. Tauber and S. Laufer (*J. Amer. Chem. Soc.*, 1941, **63**, 1488—1489).—*p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ is determined by the yellow colour developed with 0·5% of *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ in AcOH at room temp. The behaviour of other compounds is recorded. R. S. C.

Preferential reactions of polyfunctional compounds. A. J. Carter (*Iowa State Coll. J. Sci.*, 1940, **15**, 63—66).—*p*-$CN{\cdot}C_6H_4{\cdot}CO_2Me$ (I) and MgMeI (1 : 1 or 1 : 2) give *p*-$CN{\cdot}C_6H_4{\cdot}CMe_2{\cdot}OH$ (**II**), in greater yield in the latter case. (I) (1 mol.) with MgPhBr (2 mols.) gives p-*cyanotriphenylcarbinol* (**III**), m.p. 91—92°; equimol. amounts afford (?) (**III**) and a little *p*-$CN{\cdot}C_6H_4{\cdot}COPh$. (I) with LiMe (1 : 2) gives (**II**); with LiPh (1 : 1), (**III**) and *p*-$COPh{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$ are obtained. *m*-$CN{\cdot}C_6H_4{\cdot}CO_2Me$ with MgPhBr (1 : 2) gives m-*cyanotriphenylcarbinol*, m.p. 96° {whence m-*carboxytriphenylcarbinol*, m.p. 163° [*Me* ester (**IV**), m.p. 140°]}, and a little m-*benzoyltriphenylcarbinol*, m.p. 126°. Equimol. amounts of *p*-$COPh{\cdot}C_6H_4{\cdot}CO_2Me$ and MgMeBr give, after alkaline hydrolysis, p-(α-*hydroxy*-α-*phenylethyl*)*benzoic acid* (**V**), m.p. 145—146°, converted into (?) *Me* p-α-*phenylvinylbenzoate* (**VI**), m.p. 73·5—74°; MgPhBr gives (**IV**), whilst LiMe and LiPh yield (**V**) and *p*-$C_6H_4(CPh_2{\cdot}OH)_2$, respectively. *p*-$COMe{\cdot}C_6H_4{\cdot}CO_2Me$ and MgMeBr (1 : 1) give *p*-$CO_2Me{\cdot}C_6H_4{\cdot}CMe_2{\cdot}OH$, hydrolysed to *p*-$CO_2H{\cdot}C_6H_4{\cdot}CMe{:}CH_2$; with MgPhBr, (**V**) and (**VI**) are formed. *p*-$COMe{\cdot}C_6H_4{\cdot}CO_2Me$ and LiMe (1 : 1) give (?) *p*-$C_6H_4(CMe_2{\cdot}OH)_2$ in small yield, but with a 1 : 2 mixture the yield is much improved and in addition

p-COMe·C_6H_4·CMe_2·OH (**VII**) (*semicarbazone*, m.p. 213°) is formed; LiPh (1 : 1) gives p-*α-hydroxy-α-phenylethyl-triphenylcarbinol*, m.p. 138—139°, and the Me ester of (**V**). *p*-CN·C_6H_4·COPh with MgMeBr and MgPhBr gives p-(*α-hydroxy-α-phenylethyl*)*benzonitrile* (**VIII**), m.p. 91—92°, and (**III**), respectively; LiMe affords (**VIII**) and *p*-(*α*-hydroxy-*α*-phenylethyl)acetophenone (*semicarbazone*, m.p. 182—183°), whilst LiPh yields *p*-benzoyltriphenylcarbinol (**IX**) and (**III**). *p*-CN·C_6H_4·COMe with MgMeBr and MgPhBr gives (**II**) and (**VIII**), respectively; LiMe yields only (**VII**); LiPh yields p-(*α-hydroxy-α-phenylethyl*)*benzophenone*, m.p. 106° (*oxime*, m.p. 140°), and (**VIII**). *p*-COPh·C_6H_4·COCl and MgPhBr (1 : 1) yield *p*-$C_6H_4Bz_2$, *p*-carboxytriphenylcarbinol, and a little (**IX**); with excess of $CdPh_2$, *p*-$C_6H_4Bz_2$ is formed. *p*-$C_6H_4(COCl)_2$ and $CdMe_2$ (2 : 1) give *p*-COMe·C_6H_4·CO_2H and *p*-$C_6H_4Ac_2$; with $CdPh_2$, *p*-$C_6H_4Bz_2$ and *p*-C_6H_4Bz·CO_2H are formed. *o*-$C_6H_4(COCl)_2$ and $CdPh_2$ (2 : 1) give *αα*-diphenylphthalide. Sebacyl chloride and $CdMe_2$, $Cd(n\text{-}C_6H_{13})_2$, and $CdPh_2$ (2 : 1) respectively yield *αθ*-diacetyl- (**X**), *αθ-di-n-heptoyl-* (**XI**), m.p. 88° (*disemicarbazone*, m.p. 166°), and *αθ*-dibenzoyl-octane (**XII**). *θ*-Carbethoxynonoyl chloride with $CdMe_2$, $Cd(n\text{-}C_6H_{13})_2$, and $CdPh_2$ (2 : 1) respectively yield the pairs of compounds (**X**) and *κ*-ketoundecoic acid, (**XI**) and *κ*-ketopalmitic acid, and (**XII**) and *θ*-benzoylnonoic acid. CHPh:CH·COCl and ZnPhCl (1 : 1) give *γ*-benzoyl-*β*-phenyl-*γ*-benzhydrylbutyrophenone; with excess of ZnPhCl, some COPh·CH:CHPh and COPh·CH_2·$CHPh_2$ are formed. CHPh:CH·COCl and LiPh (1 : 2) yield diphenylstyrylcarbinol and COPh·CH_2·$CHPh_2$, whilst with MgPhBr (2 mols.), *ααεε*-tetraphenylpentan-*γ*-one and $CHPh_2$·CH_2·CO_2H are formed. Yields are calc. for all the reactions. The reactivities of the various groups are compared. J. L. D.

Synthesis of *cis*- and *trans*-1-methyl*cyclo*pentane-1 : 2-dicarboxylic acids and related compounds. W. E. Bachmann and W. S. Struve (*J. Amer. Chem. Soc.*, 1941, **63**, 1262—1265).—Et 2-hydroxy-2-cyano-1-methyl*cyclo*pentane-1-carboxylate (prep. from Et 2-methyl*cyclo*pentanone-2-carboxylate by HCN and 45% aq. KOH at <0°), b.p. 115—116°/2 mm., and $SOCl_2$ in C_5H_5N at 100° give Et 2-cyano-1-methyl-Δ^2-*cyclo*pentene-1-carboxylate (92%), b.p. 101—104°/2 mm., hydrolysed by boiling conc. HCl to 1-methyl-Δ^2-*cyclo*pentene-1 : 2-dicarboxylic acid (**I**), m.p. 203—204°, the *anhydride* (prep. by boiling Ac_2O), m.p. 30—32·5°, b.p. 113—115°/0·6 mm., from which in boiling MeOH gives the 2-*Me H* ester, m.p. 115—116°. Hydrogenation (PtO_2; slightly >1 atm.; EtOH) of (**I**) gives mixed acids (*A*), whence boiling Ac_2O yields the anhydride (**II**), b.p. 105—108°/6 mm., hydrolysed by aq. KOH to *cis*-1-methyl*cyclo*pentane-1 : 2-dicarboxylic acid (**III**), m.p. (bath preheated at 110°) 128—129° or (slow heating) 117—119° (cf. Dutta, *Science and Culture*, 1940, **5**, 570, 123—125°). When the Me_2 ester (prep. by CH_2N_2) of (**III**) is isomerised by boiling NaOMe–MeOH and then hydrolysed by boiling NaOH–aq. MeOH, the *trans*-acid (**IV**), m.p. 142—143·5° (*loc. cit.* 142°), is obtained. (**IV**) is also prepared from (*A*) by similar means and by conc. HCl at 180°. Ac_2O converts (**IV**) into (**II**), whence (**III**) is regenerated by hydrolysis. In boiling MeOH, (**II**) gives the cis-2-*Me H* ester (**V**), a liquid, but no H ester could be obtained from (**IV**). The acid chloride (prep. by $SOCl_2$ and a little C_5H_5N in Et_2O at room temp.) of (**V**) with the Mg derivative of $CH_2(CO_2Et)_2$ in boiling Et_2O gives *Et*$_2$ 2-*carbomethoxy*-1-*methyl*-1-cyclo*pentylformylmalonate* (80%), b.p. 170—172°/0·4 mm. (reddish-brown $FeCl_3$ colour). Treatment thereof first with NaOEt–EtOH and then with CH_2Br·CO_2Me at room temp., heating under reflux, and finally hydrolysis by boiling conc. HCl–AcOH, gives 45% of cis-*γ-keto-γ*-2-*carboxy*-1-*methyl*cyclo*pentylbutyrodilactone*,

$[CH_2]_3$  , m.p. 155—156°, partly (73%) converted by heating with aq. KOH and acidification at room temp. into cis-*γ-keto-γ*-2-*carboxy*-1-*methyl*cyclo*pentylbutyric acid* (**VI**), m.p. 114·5—115° (*Me*$_2$ ester, b.p. 172—174°/0·6 mm.). For reduction of the very resistant CO of (**VI**), catalytic hydrogenation of the ester is most promising. R. S. C.

Normal and alkamine esters of 4-methoxy*iso*phthalic acid. L. S. Fosdick and O. E. Fancher (*J. Amer. Chem. Soc.*, 1941, **63**, 1277—1279).—Oxidation (hot aq. $KMnO_4$) of 1 : 3 : 4-$C_6H_3Me_2$·OMe gives 4 : 1 : 3-OMe·$C_6H_4(CO_2H)_2$, m.p. 255—256°, the *dichloride* (prep. by $SOCl_2$), m.p. 78°, of which gives *Me*$_2$, m.p. 94°, *Et*$_2$, m.p. 57°, bis-*β*-diethyl- (*dihydrochloride*, m.p. 209—210°), *bis-β-di-n-propyl-*, decomp. 210°/<1 mm. (*borate*), and bis-*β*-di-*n*-butyl-aminoethyl (*dihydrochloride*, m.p. 120—122°), bis-*γ*-diethyl- (*dihydrochloride*, m.p. 193—195°), bis-*γ*-di-*n*-propyl- (*dihydrochloride*, m.p. 150—152°), and *bis-γ-di-n-butyl-amino-n-propyl*, decomp. 210°/<0·1 mm., 4-*methoxy*isophthalate. The toxicity of the NR_2-esters is <, and the anæsthetic efficiency of the same order as, that of procaine. R. S. C.

Mechanism of the Gattermann aldehyde synthesis. I. E. L. Niedzielski and F. F. Nord (*J. Amer. Chem. Soc.*, 1941, **63**, 1462—1463).—NaCN may replace HCN or $Zn(CN)_2$ in this synthesis. 2 mols. of HCN and >1 mol. of $AlCl_3$ are required. Reaction proceeds by way of $AlCl_3$,2HCN → $AlCl_3$,2HCN,HCl → $AlCl_3$,NH:CH·N:CHCl. 43—50% of OMe·C_6H_4·CHO is obtained from PhOMe alone or in PhEt (not in CS_2, CCl_4, $PhNO_2$, *cyclo*hexane, or PhCl), but in *o*-xylene, 3 : 4 : 1-$C_6H_3Me_2$·CHO is formed preferentially in the cold. In general PhOR do not react when NaCN or KCN is used. R. S. C.

Acylation of aldoximes. VI. Relative ease, and mechanism, of conversion of *syn*-aldoxime benzoates into nitriles in presence of pyridine and pyridinium chloride. C. R. Hauser and (Miss) G. Vermillion (*J. Amer. Chem. Soc.*, 1941, **63**, 1224—1227; cf. A., 1941, II, 226).—When *syn*-C_6H_4X·CH:N·OBz (*A*) is treated with C_5H_5N,HCl in C_5H_5N at 30±1°, the following amounts of (*A*) are recovered unchanged: X = *p*-OMe 15, *p*-Me 23, H 26, *m*-OMe 31, and *p*-Cl 48%, and under other conditions *p*-Cl 18, *m*- and *p*-NO_2 35%. The amount of ArCN formed is in inverse proportion. The mechanism is discussed. R. S. C.

Relative ease of elimination of the elements of benzoic acid from *p*-substituted *syn*-benzaldoxime benzoates in presence of triethylamine. (Miss) G. Vermillion and C. R. Hauser (*J. Amer. Chem. Soc.*, 1941, **63**, 1227—1229).—NEt_3 in C_5H_5N at 80° converts *syn-p*-C_6H_4X·CH:N·OBz (*A*) into ArCN in the following yields: X = OMe 12, Cl 48, and NO_2 95%, (*A*) being recovered in 78, 41, and 0% yield, respectively. Reaction proceeds by way of $^-$CAr:N·OBz. R. S. C.

***p*-Aldehydophenyltrimethylammonium salts and their condensation and decomposition products.** A. Zaki and W. Tadros (*J.C.S.*, 1941, 350—351; cf. A., 1930, 905).—p-*Aldehydophenyltrimethylammonium picrate* (*A*), m.p. 169° (from the methosulphate), is converted (conc. HCl) into the *chloride* (**I**), m.p. 161°, and thence into the perchlorate, m.p. 143°. *p*-NMe_2·C_6H_4·CHO (**II**) and MeI give p-*aldehydophenyltrimethylammonium iodide* (**III**), m.p. 164—165°, also obtained from (**I**) and aq. KI. (**I**) and Br–AcOH yield the chloride perbromide, m.p. 115—116° (unstable). The *oxime*, m.p. 201—202°, *semicarbazone*, m.p. 227—228°, *phenylhydrazone*, m.p. 200—201°, and m-*nitroanil*, m.p. 208°, of (*A*) are prepared from (**III**) or (**I**) and the appropriate reagent followed by aq. picric acid. Boiling NaOEt–EtOH and (**I**) afford (**II**), *p*-OEt·C_6H_4·CHO, and a little *p*-NMe_2·C_6H_4·CO_2H. A. T. P.

Reimer–Tiemann reaction of tetrahydro-β-naphthol. R. T. Arnold, H. E. Zaugg, and J. Sprung (*J. Amer. Chem. Soc.*, 1941, **63**, 1314—1316).—The aldehyde obtained from 5 : 6 : 7 : 8-tetrahydro-*β*-naphthol (**I**) (Woodward, A., 1940, II, 281; Thoms *et al.*, A., 1927, 659) is shown to be 2-*hydroxy*-5 : 6 : 7 : 8-*tetrahydro*-1-*naphthaldehyde* (**II**). Et 3-hydroxy-5 : 6 : 7 : 8-tetrahydro-2-naphthoate, b.p. 155—161°/4 mm., obtained (94% yield) by hydrogenation (Raney Ni; 140—150°/900 lb.) of 3 : 2-OH·$C_{10}H_6$·CO_2Et, is hydrolysed by alkali to the acid (**III**), m.p. 180—182°. 3-*Acetoxy*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthoyl chloride* (prep. from the OAc-acid by $SOCl_2$ in boiling C_6H_6), m.p. 90—92°, with H_2–Pd–$BaSO_4$ in xylene at 130° gives 3-*hydroxy*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthaldehyde* (**IV**), m.p. 56—57° (Cu derivative; *oxime*, m.p. 105·5—106·5°), converted into (**III**) by fusion with KOH in air at 250°. Diazotisation of 5 : 6 : 7 : 8-tetrahydro-*β*-naphthylamine by $NaNO_2$ in H_3BO_3–HF and addition to H_2SO_4 at 100° gives (**I**), m.p. 61—62°, b.p. 135°/9 mm., which with NaOH and $CHCl_3$ gives (**IV**) (trace) and (**II**), m.p 86—87° (lit. 82°). KOH-fusion of (**II**) gives 2-*hydroxy*-5 : 6 : 7 : 8-*tetrahydro*-1-*naphthoic acid* (**V**), m.p. 174—175°. 1-Bromo-5 : 6 : 7 : 8-tetrahydro-2-naphthol and KOH–Me_2SO_4 give the *Me ether*, m.p. 38—39°, the Grignard reagent from which with CO_2 yields 2-*methoxy*-5 : 6 : 7 : 8-*tetrahydro*-1-*naphthoic acid*, m.p. 148—150°, also obtained from (**V**) by KOH–Me_2SO_4. Me_2SO_4–KOH converts (**III**) into *Me* 3-*methoxy*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthoate*, m.p. 99—100°, hydrolysed by boiling 2N-KOH to the *OMe-acid*, m.p. 113—114°. R. S. C.

Synthesis of symmetrical diarylethylenes. J. H. Wood, J. A. Bacon, A. W. Meibohm, W. H. Throckmorton, and G. P. Turner (*J. Amer. Chem. Soc.*, 1941, **63**, 1334—1335).—Heating the polyarylthioaldehyde (1 pt.) with freshly reduced Cu powder for 30 min. gives the following stilbenes (temp. of heating and yields given in parentheses): (:CHPh)$_2$ (230°; 45%); 2 : 2′- (215°; trace) and 4 : 4′-dihydroxy- (220°; trace), 2 : 2′-dinitro- (160°; 0), and 3 : 4 : 3′ : 4′-tetramethoxy-stilbene (235°; 25%); αβ-di-1- (200°; 30%), and -2-naphthyl- (230°; 22%), αβ-di-2-ethoxy-1-naphthyl- (290°; 62%), *-3-phenanthryl-* (230°; 27%), m.p. 289° (corr.), *-2-methoxy-1-phenanthryl-* (275°; 71%), m.p. 277° (corr.), and *-9-anthryl-ethylene* (270°; 38%), softens at 330°, m.p. 338° (decomp.; corr.) [*dibromide*, m.p. 268° (corr.)]. Structures of new compounds are proved by oxidation. $C_{10}H_7$·CHO, HCl, and H_2S in EtOH at 0° give *poly-α-*, m.p. 155—170°, and *-β-thionaphthaldehyde*, m.p. 170—177°. *Polyphenanthrene-3-thioaldehyde*, m.p. 221°, is similarly prepared. 2-Methoxyphenanthrene, NPhMe·CHO, and $POCl_3$ at 80° give 2-methoxyphenanthrene-1-aldehyde, which with H_2S and HCl in C_6H_6–EtOAc at room temp. give the polythioaldehyde, m.p. 271°. R. S. C.

Steric inhibition of resonance in aromatic carbonyl compounds.—See A., 1941, I, 332.

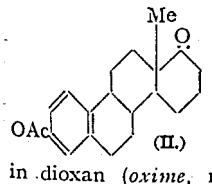
Benzanthrones. IV. Synthesis of *o*-2′- and *o*-4′-methyl-1′-naphthylbenzoic acid. Conversion of benzfluorenones into benzanthrones. F. G. Baddar (*J.C.S.*, 1941, 310—312; cf. A., 1939, II, 377).—Partly an account of work previously abstracted (A., 1940, II, 310). *o*-CO_2Me·C_6H_4·N_2Cl and 2-$C_{10}H_7Me$ in CCl_4–aq. NaOH at 0—10°, then at 45°, yield *o*-2′-methyl-1′-naphthylbenzoic acid. A mixture of acids was similarly obtained from 1-$C_{10}H_7Me$, but *1-iodo-4-methylnaphthalene*, b.p. 159°/6 mm. (from 1 : 4-$C_{10}H_6Me$·NH_2), *o*-C_6H_4I·CO_2Me, and Cu-bronze at 180—190° afford *o*-4′-*methyl*-1′-*naphthylbenzoic acid*, m.p. 200—201°. Ring-closure of the chloride of the latter acid by $AlCl_3$ gives *2-methyl-3 : 4-benzfluorenone* (**I**), m.p. 148—149° (also obtained from the acid with H_2SO_4), and 3-methyl-7-benzanthrone [this can be separated by sulphonating (**I**) with H_2SO_4]. 1 : 2 : 3-$C_{10}H_5Ph(CO)_2O$ and $AlCl_3$–NaCl at 100°, then at 140—150°, afford benzanthr-7-one-2-carboxylic acid (**II**), m.p. 347—348°, decarboxylated (Cu-bronze, quinoline) to benzanthrone (**III**). 3 : 4-Benzfluorenone-1-carboxylic acid (**IV**) is decarboxylated similarly to 3 : 4-benzfluorenone (**V**), which with $AlCl_3$–NaCl at 100°, then at 145°, yields (**III**). 1-Phenylnaphthalene-2′ : 3-dicarboxylic acid and conc. H_2SO_4 give (**II**) and a little (**IV**); the presence of (**IV**) is inferred, as decarboxylation gives (**III**) and a little (**V**) (cf. Schaarschmidt, A., 1917, i, 274). A. T. P.

Oxidation of acyloins. B. Klein (*J. Amer. Chem. Soc.*, 1941, **63**, 1474—1475).—$(COR)_2$ (R = Ph, *p*-tolyl, *p*-OMe·C_6H_4, furyl; also isatin from dioxindole) are obtained in good yield by oxidation of COR·CHR·OH with NH_4NO_3 in boiling AcOH. R. S. C.

Ketols of the *cyclo*pentanopolyhydrophenanthrene series.—See B., 1941, 111, 217.

(A) Sterols. CXXII. R. E. Marker. **(B) Origin of dehydro*iso*androsterone in urine.** L. F. Fieser and J. K. Wolfe (*J. Amer. Chem. Soc.*, 1941, **63**, 1485, 1485—1486).—Possible reduction of Δ^4-3-keto- to Δ^5-3-hydroxy-steroids is debated. R. S. C.

Steroids and sex hormones. LXVIII. *D*-Homoœstrone. M. W. Goldberg and S. Studer (*Helv. Chim. Acta*, 1941, **24**, 478—482).—Œstrone acetate is converted by KCN and AcOH in EtOH at room temp. and then at 50° into a difficultly separable mixture (**I**) of the epimeric œstrone cyanohydrin 3-monoacetates (main fraction, m.p. 160—166°, $[\alpha]_D^{17}$ +19·5° ±3° in EtOAc, from which a homogeneous *diacetate*, m.p. 225—226°, is obtained by Ac_2O and C_5H_5N at room temp.).



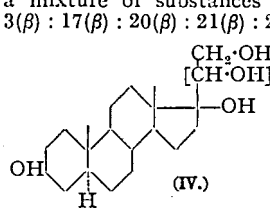
(II.)

Hydrogenation (PtO_2 in AcOH at room temp.) of (**I**) gives a mixture of 17-aminomethylœstradiol 3-monoacetates, directly converted by HNO_2 into D-*homoœstrone acetate* (**II**), m.p. 130—131°, $[\alpha]_D^{15}$ +30°±2° in dioxan. (**II**) is hydrolysed (boiling 5% KOH–MeOH) to D-*homoœstrone*, m.p. 269°, $[\alpha]_D^{18}$ +27·5°±2° in dioxan (*oxime*, m.p. 221—222°), which has only ~3% of the physiological activity of œstrone. M.p. are corr. H. W.

3 : 17 : 21-Triacetoxy-*allo*pregnan-20-one, m.p. 190—192°, and -Δ^5-pregnen-20-one, m.p. 182—185°.—See B., 1941, III, 217.

Constituents of the adrenal cortex and related substances. XLVIII. Partial synthesis of substance *L*. J. von Euw and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 418—420).—The interaction of *allo*pregnane-3(β) : 17(β) : 21-triol-20-one diacetate with MgMeBr in Et_2O–PhMe cause partial removal of Ac but gives mainly a mixture of stereoisomeric triols. The crude mixture is oxidised by HIO_4 to 3(β) : 17(β)-dihydroxy-*allo*ætiocholanic acid, m.p. 260—265° (decomp.), arising from unchanged initial material, and *allo*pregnane-3(β) : 17(β)-diol-20-one (substance *L*), characterised as the 3-monoacetate, m.p. 190—191°, $[\alpha]_D^{13}$ +14·7°±3° in $COMe_2$. H. W.

Constituents of the adrenal cortex and related substances. XLVII. Partial synthesis of *allo*pregnane-3(β) : 17(β) : 21-triol-20-one (substance *P*). J. von Euw and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 401—417).—*t*-Androsterone acetate is converted by Mg allyl bromide into *17-allylandrostane*-3(β) : 17(α)-*diol* (**I**), m.p. 176—177°, the configuration of which at $C_{(17)}$ is not established but is assumed for reasons of analogy to belong to the 17(α) series. Acetylation (Ac_2O–C_5H_5N at room temp.) transforms (**I**) into the 3-*monoacetate*, m.p. 135—136°, $[\alpha]_D^{17}$ +9·57°±2° in $COMe_2$, converted by $POCl_3$ in boiling C_5H_5N into *allohomo-*Δ$^{17:21}$*-ω-pregnadien-*3(β)*-ol acetate* (**II**), m.p. 167—168° (which shows strong selective absorption in the ultra-violet, thus establishing the conjugation of the double linkings), and an *isomeride* (**III**), m.p. 125—126°, devoid of such marked absorption. Hydroxylation of (**II**) by OsO_4–Et_2O followed by aq. Na_2SO_3 gives a mixture of substances from which *allohomo-ω-pregnane-*3(β) : 17(β) : 20(β) : 21(β) : 22-*pentaol* (**IV**), m.p. 258—259° (as semihydrate) (non-cryst. acetate), is obtained, the constitution of which is established by its conversion by HIO_4 into *t*-androsterone; the configuration at $C_{(17)}$ is established by its further transformations whereas that at $C_{(20)}$ and $C_{(21)}$ is not elucidated. $CuSO_4$ and $COMe_2$ transform (**IV**) into the 21 : 22-*CMe$_2$ ether* (**V**), m.p. 206—207°, converted by Ac_2O and C_5H_5N at 70° into its 3 : 20-*diacetate*, m.p. 213—214°, $[\alpha]_D^{14}$ +35·8°±2° in $CHCl_3$, hydrolysed by aq. AcOH at 65° to the amorphous *allo*homo-ω-pregnane-3(β) : 17(β) : 20(β) : 21(β) : 22-pentaol 3 : 20-diacetate. This is converted by aq. HIO_4 in dioxan at 15° into *allopregnane-*3(β) : 17(β) : 20(β)-*triol*-21-*al* 3 : 20-*diacetate* (**VI**), m.p. 181—182° (decomp.), $[\alpha]_D^{15}$ +36°±2° in dioxan, which reduces aq. NH_3–Ag_2O at room temp. and gives a powerful red colour with 1 : 4-$C_{10}H_6(OH)_2$ in AcOH containing HCl; it is hydrolysed ($KHCO_3$ in aq. MeOH at room temp.) to the amorphous aldehyde, m.p. 185—202° (decomp.), which is isomerised by boiling C_5H_5N and then acetylated to *allo*pregnane-3(β) : 17(β) : 21-triol-20-one 3 : 21-diacetate, m.p. 211—212°, $[\alpha]_D^{13}$ +46·1°±2° in $CHCl_3$, identical with the diacetate of substance *P* from the adrenal cortex. *allohomo-ω-*Δ^{17}*-pregnene-*3(β) : 21(α) : 22-*triol*, m.p. 176—178°, obtained as by-product of the hydroxylation of (**II**), is converted by $COMe_2$ and $CuSO_4$ into its 21 : 22-*CMe$_2$* ether, m.p. 110—112° and 131—133° after re-solidification, which yields the 3-*acetate*, m.p. 168—169°, hydroxylated (OsO_4 etc.) to an ill-defined 3(β) : 17(β) : 20(β) : 21(α) : 22-pentaol 21 : 22-*CMe$_2$* ether, m.p. 115—125° and 155—160° after re-solidification, characterised as the 3 : 20-*diacetate*, m.p. 230—231°, $[\alpha]_D^{14}$ +1·8°±2° in $CHCl_3$. This is transformed by cautious hydrolysis with dil. AcOH into the *pentaol diacetate*, m.p. 134—137°, degraded by HIO_4 to (**VI**). (**III**) is converted by OsO_4 etc. into a (?) *pentaol*, $C_{22}H_{38}O_5$, m.p. 230—231°, which gives acid products exclusively when oxidised by CrO_3. Acetonisation and acetylation of the by-products from (**IV**) yields (probably) the 3-monoacetate, m.p. 208—211°, of (**V**), hydrolysed to the (?) 3-*monoacetate*, m.p. 242—243·5°, $[\alpha]_D^{14}$ −12·0°±2° in $CHCl_3$, of (**IV**). M.p. are corr. H. W.



(IV.)

Constituents of the adrenal cortex and related substances. XLV. Δ^4-Pregnen-20-ol-21-al-3-one. W. Schindler, H. Frey, and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 360—374).—Δ^5-Pregnen-3-ol-21-al-20-one Me_2 acetal is reduced by $Al(OPr^\beta)_3$ and $Pr^\beta OH$–PhMe to Δ^5-*pregnene*-3 : 20-*diol*-21-*al Me$_2$ acetal* (**I**), m.p. 135—136°, $[\alpha]_D^{16}$ −48°±2° in MeOH,

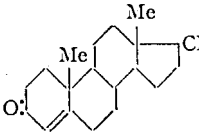
converted by gentle acetylation (Ac_2O in C_5H_5N at room temp.) into the 3-*monoacetate*, m.p. 122·5—123°, $[\alpha]_D^{20}$ −21·4° ±3° in $COMe_2$, and by more drastic treatment into the *diacetate*, m.p. 185—186°, $[\alpha]_D^{17}$ −21·5°±2° in $COMe_2$, which is hydrolysed by boiling KOH–MeOH to (I) and by K_2CO_3 in aq. MeOH at room temp. to the 20-*monoacetate*, m.p. 151—152°, $[\alpha]_D^{17}$ −17°±2° in MeOH. The latter substance is oxidised [$Al(OBu^{\gamma})_3$ and $COMe_2$ in C_6H_6] to Δ^4-*pregnen*-20-*ol*-21-*al*-3-*one* Me_2 *acetal* 20-*acetate* (II), m.p. 112—113°, $[\alpha]_D^{15}$ +111°±4° in MeOH, hydrolysed by acid or alkali to the free *hydroxyacetal* (III), m.p. 135—136°, $[\alpha]_D^{18}$ +62·1°±2° in $COMe_2$ [*semicarbazone*, m.p. 220—222° (decomp.)], more simply obtained from (I) by partial oxidation (Oppenauer) and acetylated to (II). The spectra of (II) and (III) in EtOH show strong selective absorption. Hydrolysis by HCl in dil. AcOH converts (III) into Δ^4-*pregnen*-20-*ol*-21-*al*-3-*one* (IV), m.p. 206—208° (decomp.), $[\alpha]_D^{20}$ +84°±2° in dioxan (*disemicarbazone*, m.p. >300° after darkening >200°), which is probably bimol. (as dioxan derivative) or termol.; in solution there is probably an equilibrium with the unimol. variety since unimol. (III) is obtained with HCl–EtOH. Boiling C_5H_5N in CO_2 causes isomerisation of (IV) to deoxycorticosterone (VI), isolated as the acetate (VII), m.p. 161—162·5°. Ac_2O and C_5H_5N transform (IV) at room temp. into the *acetate* (V), m.p. 255—256° (slight decomp.), $[\alpha]_D^{20}$ +56°±2° in dioxan, which is certainly not unimol. since it has a high m.p., is very sparingly sol. in Et_2O, EtOH, or $COMe_2$, and cannot be sublimed below 230° in a high vac. Determinations of mol. wt. (Rast) in camphor indicate termol. form. (IV) and (V) reduce aq. NH_3–Ag_2O solution at room temp. somewhat less readily than do (VI) and (VII), and also give a positive aldehyde reaction with 1 : 4-$C_{10}H_6(OH)_2$ in HCl–AcOH. This reaction is positive with all OH-aldehyde acetals. Δ^5-Pregnen-3-ol-21-al-20-one, EtSH, and HCl give the *Et*$_2$ *mercaptal*, m.p. 124—125°, $[\alpha]_D^{21}$ +137·6°±3° in $COMe_2$ (accompanied by 3-hydroxy-Δ^5-ætiocholenic acid, m.p. 264—266°). This is converted by Ac_2O and C_5H_5N at 20° into the *acetate*, m.p. 130—132°, $[\alpha]_D^{17}$ +149·5°±3° in $COMe_2$, and oxidised by $Al(OBu^{\gamma})_3$ and $COMe_2$ in C_6H_6 to Δ^4-*pregnen*-21-*al*-3 : 20-*dione* *Et*$_2$ *mercaptal*, m.p. 94—96°, $[\alpha]_D^{20}$ +258·2°±6° in $COMe_2$, which could not be satisfactorily reduced to the diol. M.p. are corr. H. W.

Constituents of the adrenal cortex and related substances. XLIV. Δ^{11}-Dehydroprogesterone. C. W. Shoppee and T. Reichstein (*Helv. Chim. Acta*, 1941, **24**, 351—360).—11-Hydroxyprogesterone is converted by boiling AcOH–conc. HCl into $\Delta^{4:11}$-*pregnadiene*-3 : 20-*dione* (I), m.p. 120—122° (or 117—122° if very finely divided), $[\alpha]_D^{18}$ +145°±5°, $[\alpha]_{5461}^{18}$ +184·5°±2·5° in $COMe_2$, which is hydrogenated (H_2–PtO_2–AcOH) and then oxidised (CrO_3, AcOH) to *allo*pregnane-3 : 20-dione, m.p. 200—201°, with a small proportion of pregnane-3 : 20-dione. 3(α)-Hydroxy-12-acetoxypregnan-20-one is oxidised by CrO_3 in AcOH at 20° to 12-acetoxypregnane-3 : 20-dione, new m.p. 132—134°, hydrolysed by KOH–MeOH to 12-*hydroxypregnane*-3 : 20-*dione*, m.p. 182—184°, $[\alpha]_D^{17}$ +135°±2·5°, $[\alpha]_{5461}^{17}$ +164°±2·5° in EtOH. This is converted by Br in AcOH containing a little HBr followed by boiling C_5H_5N into 12-hydroxyprogesterone, m.p. 164—167° and 195—198° after re-solidification, $[\alpha]_D^{15}$ +205°±4°, $[\alpha]_{5461}^{15}$ +239°±4° in $COMe_2$. M.p. are corr. (I) possesses progesterone activity. H. W.

Isolation of 17-hydroxyprogesterone from the adrenal gland. J. J. Pfiffner and H. B. North (*J. Biol. Chem.*, 1941, **139**, 855—861).—The isolation of Δ^4-*pregnen*-17-*ol*-3 : 20-*dione* (I) [17-(? β)-*hydroxyprogesterone*], m.p. 212—215°, $[\alpha]_D^{27}$ +102°±3° in $CHCl_3$, absorption max. at 242 mμ. [*disemicarbazone*, darkens ~240°, sinters 280—290°; *dioxime*, m.p. 250—251° (decomp.) (sinters ~240°)], is described. The yield is 1·4 g. of crude product from ~3 tons of ox glands. (I) does not react with Ac_2O in C_5H_5N at room temp.; it is oxidised by CrO_3–AcOH to Δ^4-androstene-3 : 17-dione. Doses of ⩾ 5 mg. of (I) seem to have no progestational effect on rabbits and it also has no cortical hormonal action. The androgenic activity in the castrated rat is comparable with that of androsterone and adrenosterone; on the capon it appears to have no such activity. W. McC.

Steroids and sex hormones. LXVII. Preparation of a homologue of progesterone. P. A. Plattner and W. Schreck (*Helv. Chim. Acta*, 1941, **24**, 472—477).—$\Delta^{5:17}$-3-Hydroxypregnadiene-21-carboxylic acid is converted by C_5H_5N and Ac_2O at room temp. into the non-cryst. acetate and thence by $SOCl_2$ in C_6H_6 into the corresponding *chloride*, m.p. 189—190°, $[\alpha]_D$ −84°±3°. This is transformed by ZnMeI into Δ^5-3-*acetoxy*-17-β-*ketopropylideneandrostene* (I), m.p. 189—190°, $[\alpha]_D$ −63°±3°, which is reduced (H_2, Raney Ni, EtOH) to Δ^5-3-*acetoxy*-17-β-*ketopropylandrostene*, m.p. 156—157°, $[\alpha]_D$ −49°±4°, hydrolysed (K_2CO_3 in boiling 80% MeOH) to the 3-*OH*-derivative (II), m.p. 177—178°, $[\alpha]_D$ −48°±4°. Oxidation of (II) by $Al(OBu^{\gamma})_3$ in $COMe_2$–C_6H_6 at room temp. leads to Δ^4-3-*keto*-17-β-*ketopropylandrostene*, m.p. 153—154°, $[\alpha]_D$ +89°±2°, which is biologically inactive. Hydrolysis (K_2CO_3 in boiling 80% MeOH) of (I) affords Δ^5-3-*hydroxy*-, m.p. 168—169°, $[\alpha]_D$ −65°±2°, oxidised by $Al(OBu^{\gamma})_3$ to Δ^4-3-*keto*-17-β-*ketopropylideneandrostene*, m.p. 176—177°, $[\alpha]_D$ +87°±2°. M.p. are corr. $[\alpha]_D$ are in dioxan. H. W.

Steroids. XXIX. Higher homologues of progesterone and deoxycorticosterone acetate. A. Wettstein (*Helv. Chim. Acta*, 1941, **24**, 311—317).—Δ^5-3*t*-Acetoxybisnorcholenic acid is converted by $SOCl_2$ at room temp. into the chloride (I), which with ZnMeI yields Δ^5-3t-*acetoxynorcholen*-22-*one*, m.p. 177—178°, hydrolysed (K_2CO_3 in aq. MeOH at 100°) to Δ^4-*norcholen*-3t-*ol*-22-*one*, m.p. 179—181°, which is oxidised [$Al(OPr^{\beta})_3$ and *cyclo*hexanone in boiling PhMe] to Δ^5-*norcholene*-3 : 22-*dione* (II) (A; R = Me), m.p. 213—215°. (I) and CH_2N_2 in CH_2Cl_2 at −10° afford (impure) Δ^5-23-*diazo*-3t-*acetoxynorcholen*-22-*one*,



(A.)

m.p. ~260—265°, converted by KOH–MeOH at 17° followed by H_2O at 0° into the 3*t*-OH-derivative, which with anhyd. KOAc and glacial AcOH at 98° gives Δ^5-3t-*hydroxy*-23-*acetoxynorcholen*-22-*one*, m.p. 152—153°. This is acetylated (Ac_2O–C_5H_5N at room temp.) to the 3t : 23-*diacetate*, dimorphous, m.p. ~164—165° and 171—172°, and oxidised by $Al(OPr^{\beta})_3$ and *cyclo*hexanone in PhMe to Δ^4-23-*acetoxynorcholene*-3 : 22-*dione* (III) (A; R = CH_2·OAc), m.p. 167—168°. M.p. are corr. Since (II) and (III) are physiologically inactive, the insertion of CHMe between nucleus and side-chain in progesterone and deoxycorticosterone is sufficient to destroy the sp. hormonal activity of these compounds. H. W.

Quinonyl derivatives of fatty acids. L. F. Fieser, M. D. Gates, jun., and G. W. Kilmer (*J. Amer. Chem. Soc.*, 1940, **62**, 2966—2970).—Clemmensen–Martin reduction of 2 : 5 : 1-$(OMe)_2C_6H_3$·CO·$[CH_2]_2$·CO_2H [prep. in 57·2% yield from *p*-$C_6H_4(OMe)_2$ by $(CH_2$·$CO)_2O$ (I) and $AlCl_3$ in $(CHCl_2)_2$–$PhNO_2$ at, first, 5° and then room temp.], m.p. 101—102°, gives γ-2 : 5-*dimethoxyphenylbutyric acid* (41·8%), m.p. 66—66·8°, which could not be demethylated and with CrO_3 at 60° or 20° gives a *substance*, m.p. 222—223° (decomp.). The Friedel–Crafts reaction of quinol and (I) in $PhNO_2$–$(CHCl_2)_2$ at 55° and subsequent heating at 130—135° gives γ-*keto*-o- (II) (20%), m.p. 140·4—140·8° after softening, and -*p*-hydroxyphenyl-*n*-butyric acid (3—5%), m.p. 154—156°. (II) yields (Clemmensen–Martin) *o*-OH·C_6H_4·$[CH_2]_3$·CO_2H (96%), m.p. 64—67·5°, which by successive condensation with *p*-SO_3H·C_6H_4·N_2Cl (III) in NaOH at 0°, reduction by $Na_2S_2O_4$ at 70°, and oxidation by $Na_2Cr_2O_7$–H_2SO_4 at 5° gives γ-p-*benzoquinonyl*-n-*butyric acid* (57%) (IV), m.p. 104·9—105·3° (corresponding *quinol-acid*, m.p. 131·2—132° after softening). $(CH_2{:}CH)_2$ and (IV) in C_6H_6 at 65—70° give γ-5 : 8 : 9 : 10-*tetrahydro*-1 : 4-*naphthaquinone*-2-n-*butyric acid* (86%), m.p. 124·5—125·5°, isomerised by HCl–AcOH to γ-1 : 4-dihydroxy-5 : 8-dihydro-2-naphthyl-*n*-butyric acid, m.p. 171—173°, and converted in one reaction by a drop of H_2SO_4 in AcOH at 100° and then CrO_3–AcOH at 40° (later 60—65°) into 1 : 4-*naphthaquinone*-2-γ-n-*butyric acid*, m.p. 151·3—152°. *o*-OH·C_6H_4·CO·$[CH_2]_4$·CO_2H (von Braun, A., 1923, i, 104) affords similarly ε-o-*hydroxyphenyl*-n-*hexoic acid*, m.p. 89—90·5°, the derived 5-NH_2-acid (*hydrochloride*, cryst.), ε-p-*benzoquinonyl*-n-*hexoic acid* (83%), m.p. 101·4—102° (derived *quinol-acid*, m.p. 96·8—97·6°), and 5 : 8 : 9 : 10-*tetrahydro*-1 : 4-*naphthaquinone*-2-ε-n-*hexoic acid* (V) (75%), m.p. 102·8—103·6°. With a little HCl and a trace of $SnCl_2$ in boiling EtOH, (V) gives ε-1 : 4-*dihydroxy*-5 : 8-*dihydro*-2-*naphthyl*-n-*hexoic acid*, m.p. 154—154·8°, also obtained by boiling $Na_2S_2O_4$–30% KOH–N_2 from the *Et* ester (prep. by HCl–EtOH), m.p. 95—96°, of (V) and oxidised by CrO_3–AcOH at 60° to 1 : 4-*naphthaquinone*-2-ε-n-*hexoic acid*, m.p. 146—147·5° after softening. M.p. are corr. R. S. C.

Mills–Nixon effect. II. R. T. Arnold and H. E. Zaugg (*J. Amer. Chem. Soc.*, 1941, **63**, 1317—1320; cf. A., 1940, II, 166).—Coupling of *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$ with 5 : 6 : 7 : 8-tetrahydro-α-naphthol, reduction by $Na_2S_2O_4$, and oxidation by MnO_2–H_2SO_4 gives 5 : 6 : 7 : 8-tetrahydro-1 : 4-naphthaquinone (60% over-all yield), m.p. 55—56° (derived quinol, m.p. 178—179°), which has an oxidation–reduction potential (E_0) 0·585 (potentiometric or polarographic). *o*-Xyloquinone (similar prep.), m.p. 56·5—57·5° [derived quinol, m.p. 223—224° (decomp.)], has E_0 0·588 (potentiometric) or 0·589 (polarographic). 4-Nitrohydrindene (modified prep.) is hydrogenated (Rancy Ni; 150°/800—1300 lb.; 94% yield) to the amine, which yields (diazo-reaction; KI) 4-hydroxy- (**I**), m.p. 49—50°, and impure 4-iodo-hydrindene [converted into (**I**) by aq. NaOH + Cu at 275°]. Hydrindene and $ClSO_3H$ at −10° give 76% of 5-, m.p. 46—47° (lit. 45°) (amide, m.p. 135—136°), and 4-sulphonyl chloride (**II**), m.p. 53—53·5° [amide, m.p. 118—119°; Spilker's compound, m.p. 91—92° (A., 1893, i, 518), was a eutectic mixture of 4- and 5-sulphonamides]. Hydrolysis of (**II**) by boiling H_2O gives the 4-sulphonic acid; the Na salt is converted by addition to KOH at 250—280°, later heating at 305° and finally at 270—285°, into (**I**) (80%), forms, m.p. 39·5—40° and 49—50°. This yields, as above, 7-*amino*-4-*hydroxyhydrindene* (93%), m.p. ~205° (decomp.) (sublimes at 160°), and thence (MnO_2–H_2SO_4 66%; $FeCl_3$–HCl 40%) 4 : 7-*hydrindenequinone*, m.p. 41—42° [derived *quinol* (**III**), m.p. 184—185°; *quinhydrone*, m.p. 98—99°], which has E_0 0·641 (potentiometric) or 0·638 (polarographic). β-2 : 5-Dimethoxyphenylpropionic acid (prep. from the cinnamic acid by H_2–PtO_2 in AcOH–95% EtOH), m.p. 65—66°, with P_2O_5 in boiling C_6H_6 gives 4 : 7-*dimethoxy*-1-*hydrindone*, m.p. 124·5—125°, reduced by H_2–Raney Ni in 95% EtOH at 150°/1400 lb. to 4 : 7-*dimethoxyhydrindene*, m.p. 85—85·5°, also obtained from (**III**) by Me_2SO_4. From E_0 it is concluded that a Mills–Nixon partial fixation of ethylenic linkings is shown in the hydrindene- but not in the tetrahydronaphtha-quinone series. R. S. C.

Production and separation of isomeric aminohydroxyanthraquinones.—See B., 1941, II, 254.

3 : 7-Dihydroxy-1 : 2 : 5 : 6-dibenzanthraquinone. J. Cason and L. F. Fieser (*J. Amer. Chem. Soc.*, 1941, **63**, 1256—1258).—4-*Methoxy*-2-*naphthoic acid* (**I**), m.p. 202—202·5° [prep. from 4' : 2-OH·$C_{10}H_6{\cdot}CO_2H$ (**II**) (Cason, A., 1941, II, 169) by Me_2SO_4–NaOH], does not undergo intermol. condensation with H_2SO_4 or HF. The derived (PCl_5; 100°) acid chloride with $AlCl_3$ in $PhNO_2$ (not CS_2) at room temp. gives 3 : 7-*dimethoxy*-1 : 2 : 5 : 6-*dibenzanthraquinone* (29%), m.p. 347—349° (vac.), and a small amount of 3-*carboxy*-α-*naphthyl* 4-*methoxy*-2-*naphthoate*, m.p. 259·7—260·2° [Na salt; structure proved by hydrolysis to (**I**) and (**II**)]. Demethylation by $AlCl_3$ in boiling C_6H_6 gives the $(OH)_2$-*quinone* [*diacetate*, m.p. 316—319° (decomp.; vac.); yellow in alkali], which differs from the dibenzanthracene metabolite excreted by rabbits (cf. A., 1941, II, 9). M.p. are corr. R. S. C.

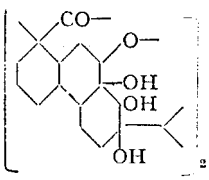
III.—TERPENES.

Isomerisation in the Bouveault–Blanc reduction of methyl hydrogen camphorates. W. W. Crouch and H. L. Lochte (*J. Amer. Chem. Soc.*, 1941, **63**, 1331—1334).—*o*-Me H *iso*camphorate is not hydrogenated in methyl*cyclo*hexane or dioxan in presence of Cu chromite at 250°/5000 lb. With Na–EtOH it gives *d*-camphoric (**I**), *iso*camphoric (**II**), *cis*-[isolated as α-campholide (**III**), m.p. 213° (lit. 210—212°)], and trans-*hydroxycampholic acid* (**IV**), m.p. 112—113° (*acetate*, m.p. 55—56°; not lactonised by boiling N-HCl), and a small amount of an acid (**V**), m.p. 217—218°. Similar reduction of (*a*) *o*- or (*b*) *allo*-Me H camphorate causes no such isomerisation, yielding (*a*) (**I**), (**II**), (**III**), (**V**) (m.p. 218—219°), and β-campholide (3%), and (*b*) in poor yields (**I**), (**III**), (**VI**), and *allo*-Et H camphorate, respectively. (**V**) is obtained also by heating (**II**) and (**IV**) at 175°. R. S. C.

Wagner–Meerwein rearrangement. Catalytic action of phenols in the isomerisation of camphene hydrochloride. P. D. Bartlett and J. D. Gill, jun. (*J. Amer. Chem. Soc.*, 1941, **63**, 1273—1277).—Catalysts for the change, camphene hydrochloride (**I**) → *iso*bornyl chloride, owe their activity to their action as donors of Cl^-. To measure the activity of phenols for this change, it is necessary to suppress the much stronger effect of the HCl liberated by dissociation of (**I**). This is effected by the presence of an excess of camphene (**II**). Since the rate of isomerisation is ≪ that of the change, (**II**) + HCl ⇌ (**I**), rates of isomerisation are measurable when a known deficiency (~50%) of gaseous HCl is passed into (**II**) and the phenol in $PhNO_2$; allowance (method detailed) is made for catalysis by the small remaining amount of HCl. First-order *k* for the phenol-catalysed reaction accord with the equation, $k = a[P] + b[P]^2$, in which P = the phenol used. This indicates independent reactions involving one and two mols. of phenol, respectively. Relative effects are *p*-CN·$C_6H_4{\cdot}OH$ > PhOH > *o*-cresol ≫ picric acid, *i.e.*, the order in hydrolysis of *p*-OMe·$C_6H_4{\cdot}CHPhCl$ in $PhNO_2$ and the order of H bonding powers and (except for *o*-compounds) of acid strengths. Phenols thus act on the Cl of (**I**), solvating the Cl^- by H linkings. Two mechanisms of the reaction involving 2 mols. of phenol are discussed. R. S. C.

Diterpenes. XLVI. Dimeric inner ester of tetrahydroxyabietic acid and its further degradation. M. Ruzicka and L. Sternbach (*Helv. Chim. Acta*, 1941, **24**, 492—501).—Determinations of the mol. wt. of "tetrahydroxyabietolactone" [*diacetate*, m.p. ~290°, obtained by use of Ac_2O and C_5H_5N at room temp. or by NaOMe and boiling Ac_2O; not oxidised by $Pb(OAc)_4$] and its oxidation products show the presence of dimeric substances. The "lactone" is therefore a dimeric inner ester of tetrahydroxyabietic acid, shown by its formation from the oxidodihydroxy-acid and the products of its oxidation to be (**I**). This is transformed by oxidation with 2 mols. of $Pb(OMe)_4$ per abietic acid residue with loss of 1 C per residue into the *dimeric inner diketo-ester* (**II**), m.p. 162—164°, also obtained by use of CrO_3 (≡4—6 O) in hot AcOH; only the CO groups in the side-chain are active (*di*-p-*nitrophenylhydrazone*, m.p. 275—277°), that in ring c being greatly

(I.)



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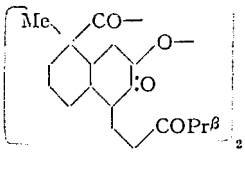
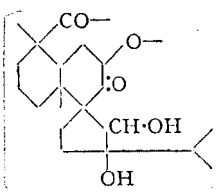
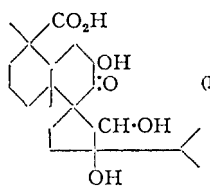


hindered sterically. Cryst. products are not obtained by the oxidation of (**I**) with $Pb(OAc)_4$ (1 mol. per abietic acid residue) under mild conditions but if the solution is subsequently boiled or if the product is treated with hot AcOH or KOH–EtOH a cryst. *dimeric inner ester* of a *ketotrihydroxy-acid* (**III**), m.p. 245—246° (*diacetate*, m.p. ~300°), is obtained in very good yield. This does not react with NH_2OH or $NHPh{\cdot}NH_2$. On similar grounds the ketotrihydroxyabietic acid obtained by oxidising α-tetrahydroxyabietic acid with 1 mol. of $Pb(OAc)_4$ is now regarded as (**IV**). Oxidation of (**III**) with CrO_3 (≡1 O) gives the dimeric *inner ester* of a *dihydroxydiketo-acid* (**V**), m.p. ~290—291°, which does not give cryst. compounds when hydrolysed by alkali, does not yield an Ac derivative, and does not react with carbonyl reagents. M.p. are corr. H. W.

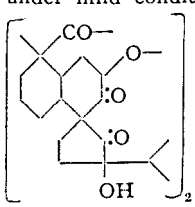
(III.)



(IV.)

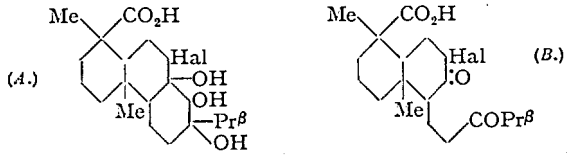


(V.)

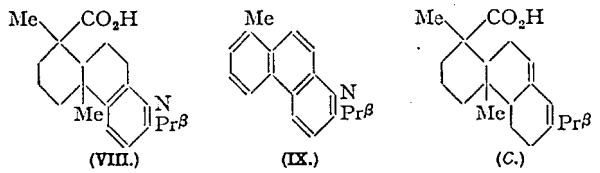


Diterpenes. XLVII. Halogenotrihydroxyabietic acids and their further transformations into 8-azaretene. L. Ruzicka, L. Sternbach, and O. Jeger (*Helv. Chim. Acta*, 1941, **24**, 504—515).—Abietic acid (**I**) is oxidised by $KMnO_4$ and the Ba salt of the product is converted by HBr in presence of Et_2O into *bromotrihydroxyabietic acid* (**II**) (cf. *A*), m.p. 148—149°. *Iodotrihydroxyabietic acid* (**III**) (cf. *A*) is obtained similarly or, preferably, by the action of dil. HI on the Na salt of (**II**) or of chlorotrihydroxyabietic acid (**IV**). Oxidation of (**IV**) by $Pb(OAc)_4$ (2 mols.) in AcOH–$CHCl_3$ yields the *chlorodiketo-acid* (cf. *B*), m.p. 157—158° (*monosemicarbazone*, m.p. 204—

206°; the second CO is sluggish). Similar treatment of (**II**) and (**III**) gives the *bromo-* (**V**), m.p. 138—145° according to

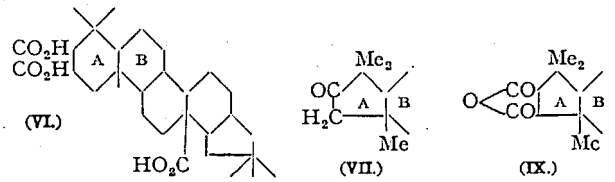


the rate of heating (also obtained by use of CrO_3 in AcOH), and the *iodo-* (**VI**), m.p. 117—119° (decomp.), *-diketo-acid* (cf. *B*). Mild treatment with HI followed by $Na_2S_2O_3$ dehalogenates (**VI**) to the *diketo-acid* (**VII**), m.p. 123—124°, which yields only a *monophenylhydrazone*, m.p. 191—192°, but is shown by its absorption spectrum to contain 2 CO. Hydrogenation (PtO_2 in AcOH) of this acid causes the absorption of 2 H_2 but the expected $(OH)_2$-acid passes into the *oxido-acid*, $C_{19}H_{32}O_3$, m.p. 142—147°. Conc. aq. NH_3 at room temp. converts (**VII**) into *azadehydroabietic acid* (**VIII**), m.p. 258—260° (stable *picrate*, m.p. 221—223°), the constitution of which is confirmed by the absorption spectrum. Similarly, (**V**) or (**VI**) is transformed by NH_3 into *ketoazadehydroabietic acid*, m.p. 284—287° (*picrate*, m.p. 190—192°),



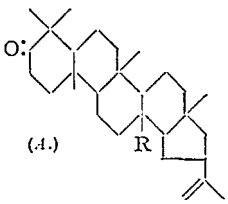
catalytically reduced to the *OH-acid*, $C_{19}H_{27}O_3N$, m.p. 205—206° (vac.), and converted by N_2H_4,H_2O and NaOEt at 180—200° into (**VIII**). Se at 330—340° dehydrogenates and decarboxylates (**VIII**) to *8-azaretene* (**IX**), m.p. 117·5—118·5° [*picrate*, m.p. 190—195° (decomp.); addtive compound with $C_6H_3(NO_2)_3$, m.p. 100—101°]. The smooth conversion of (**I**) into (**IX**) justifies the placing of the double linkings in (**I**) according to (*C*). M.p. are corr. H. W.

Triterpenes. LIX. Two new methods of converting dihydrobetulin into dihydrobetulonic acid and degradation of the latter in ring A. L. Ruzicka, M. Brenner, and E. Rey (*Helv. Chim. Acta*, 1941, **24**, 515—529).—Betulin is converted by H_2 at ~180°/100 atm. in EtOH containing Raney Ni into dihydrobetulin, m.p. 276—277°, converted by dehydrogenation with Cu-bronze at 250—320° followed by oxidation with $KMnO_4$ into dihydrobetulonic acid (**I**), m.p. 276—277°, and a *ketone*, $C_{29}H_{48}O$ (**II**), m.p. 208—209° after softening at 206°, $[\alpha]_D$ +80° in $CHCl_3$ [*oxime*, m.p. 280° (decomp.); *semicarbazone*, m.p. ~270°; *m-nitrobenzylidene* derivative, m.p. 163—164°]. Reduction (PtO_2 in AcOH) of (**II**) affords the *carbinol* (**III**), $C_{29}H_{50}O$, m.p. 171—173°, $[\alpha]_D$ +37° in $CHCl_3$ (*acetate*, m.p. 206—208°, $[\alpha]_D$ +45° in $CHCl_3$; *tribromoacetate*, m.p. 232°). Decarboxylation of *dihydrobetulic acid* (**II**) (Cu powder at 300°) gives an unsaturated *ketone* (or mixture), $C_{29}H_{46}O$, m.p. 167—170° after softening, $[\alpha]_D$ +50° in $CHCl_3$, hydrogenated (Pb in AcOH) to (**III**). Betulin monoacetate is reduced (PtO_2 in EtOH–AcOH–dioxan) to *dihydrobetulin monoacetate* (**V**), m.p. 258—259°, $[\alpha]_D$ −5·1° in $CHCl_3$, oxidised (CrO_3 in AcOH at room temp.) to acetyldihydrobetulic acid, m.p. 311—312·5°, $[\alpha]_D$ −11·3° in $CHCl_3$ (Me ester, m.p. 238·5—239°, $[\alpha]_D$ −12·5° in $CHCl_3$), hydrolysed (KOH–MeOH) to (**IV**), m.p. 323—324°, $[\alpha]_D$ −28·2° in dioxan (*Me* ester, m.p. 239° after softening at 234°, $[\alpha]_D$ −18·9° in $CHCl_3$), which is oxidised (CrO_3 in AcOH) to (**I**) (overall yield, 50—60%). (**V**) is transformed by $MeSO_2Cl$ in C_5H_5N at −4° into the *methanesulphonate*, m.p. 165—166° (decomp.), converted by NaI in dry $COMe_2$ at 135° into an unsaturated *substance*, $C_{32}H_{52}O_2$, m.p. 231—234° (not const.), $[\alpha]_D$ −54° in $CHCl_3$. (**I**) is oxidised to the tricarboxylic acid (**VI**), m.p. 276—277°, $[\alpha]_D$ −8·4° in EtOH, quantitatively cyclised at 270°/11 mm., to *A*-nordihydrobetulonic acid (**VII**), m.p. 258—259°, $[\alpha]_D$ +86·3° in $CHCl_3$ [Me ester (**VIII**), $[\alpha]_D$ +84·6° in $CHCl_3$]. Oxidation of (**VII**) by SeO_2 in dioxan at 220° gives the *tricarboxylic anhydride* (**IX**), m.p. 310—311°, converted by CH_2N_2 in Et_2O into the *Me* ester, m.p. 269—270°, $[\alpha]_D$ +42·5° in $CHCl_3$, also obtained by the direct oxidation of (**VIII**) by SeO_2 in dioxan at 200°. (**IX**) is hydrolysed to the tricarboxylic *acid* (**X**), m.p. 260° (slight decomp.) after softening (*Me_3* ester, m.p. 123—124°, $[\alpha]_D$ ±0° in $CHCl_3$), reconverted by Ac_2O into (**IX**).



(**X**) shows the behaviour typical of a substituted glutaric acid obtained from a five-membered ring ketone, thus affording further evidence of the six-membered nature of ring A in betulin. M.p. are corr. and determined in closed capillaries. H. W.

Triterpenes. LX. Oxidations of the alcoholic groups of betulin. L. Ruzicka and E. Rey (*Helv. Chim. Acta*, 1941, **24**, 529—536).—Dehydrogenation of betulin (**I**) with Cu powder at 300° gives *betulonealdehyde* (**II**) (*A*; R = CHO), m.p. 165—166°, $[\alpha]_D$ +52·4° in $CHCl_3$ (*dioxime*, m.p. 247°), reduced by N_2H_4,H_2O in boiling EtOH to α-lupene, m.p. 164°, $[\alpha]_D$ +30·3° in $CHCl_3$. Oxidation of (**I**) by $Al(OBu^{\nu})_3$ in boiling C_6H_6 containing *p*-benzoquinone yields (**II**) and *lupenol-2-one*, (cf. *A*; R = CH_2·OH), m.p. 188—189°, $[\alpha]_D$ +54° in $CHCl_3$, the constitution of which follows from its difference



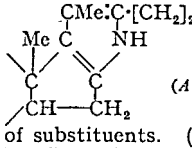
from the only possible alternative, *betulinaldehyde* [*2-hydroxylupenol*], m.p. 192—193°, $[\alpha]_D$ +19·2° in $CHCl_3$, obtained by hydrolysis of its acetate. Under very mild conditions CrO_3 oxidises (**I**) to (**II**) with minor proportions of betulonic acid (**III**), identified as the Me ester (**IV**), m.p. 165°, $[\alpha]_D$ +31·4° in $CHCl_3$ [*oxime*, m.p. 238° (decomp.)], and small amounts of a *substance*, $C_{31}H_{48}O_3$, m.p. 198°, $[\alpha]_D$ +15·8° in $CHCl_3$, which gives a yellow colour with $C(NO_2)_4$. (**III**) is also obtained by the gentle oxidation of (**II**) with $KMnO_4$. Hydrogenation (PtO_2 in AcOH) of (**IV**) affords Me dihydrobetulate, m.p. 238—239°. (**IV**) is reduced by N_2H_4,H_2O and NaOEt–EtOH at 200° to *Me 2-deoxybetulinate*, m.p. 153°, $[\alpha]_D$ +2·1° in $CHCl_3$. M.p. are corr. and determined in sealed but not evacuated capillaries. H. W.

Sterols. CX. Position of the hydroxyl groups in chlorogenin. R. E. Marker, E. M. Jones, D. L. Turner, and E. Rohrmann (*J. Amer. Chem. Soc.*, 1940, **62**, 3006—3009).—The positions of the 5 : 6-ethylenic linking in diosgenin (**I**) and the 3- and 6-OH of chlorogenin (**II**) are confirmed. Oxidation (CrO_3; 25—28°) of *ψ-chlorogenin* (**III**), m.p. 267—270°, or its H_2-derivative (**IV**) gives Δ^{16}-allo*pregnene*-3 : 6 : 20-*trione* (**V**), m.p. 223—226°. That of (**I**) at 15—20° gives chlorogenone (**VI**). *ψ*-Chlorogenone, an oil, is obtained from (**VI**) by Ac_2O at 200° and later 2% KOH–EtOH, is reconverted into (**VI**) by HCl–EtOH, reduced by Na–EtOH to (**III**), and hydrogenated (PtO_2; EtOH; 45 lb.) to a product, which is oxidised to allo*pregnane*-3 : 6 : 20-*trione* (**VII**), m.p. 232—235°, also obtained from (**VI**) by H_2–Pd–$BaSO_4$–EtOH at 15 lb. When the diacetate of (**IV**) is oxidised (CrO_3), then hydrolysed (2% KOH), and hydrogenated (Pd–$BaSO_4$; EtOH), allo*pregnane*-3 : 6-*diol*-20-*one*, m.p. 206—209°, is formed. (**IV**) is obtained from (**III**) by successive treatment with boiling Ac_2O, CrO_3–AcOH at 25—28°, H_2–PtO_2, CrO_3–AcOH, and KOH–EtOH. *ψ*-Diosgenin with CrO_3 at 25—28° gives Δ^{16}-*allo*pregnen-3 : 6 : 20-trione and with Zn–Hg–EtOH–HCl gives *allo*pregnane. Δ^5-*allo*Pregnen-3-ol-20-one and CrO_3 give (**VII**). R. S. C.

Sterols. CXI. Sapogenins. XL. Conversion of chlorogenin into tigogenin. R. E. Marker, D. L. Turner, and P. R. Ulshafer (*J. Amer. Chem. Soc.*, 1940, **62**, 3009—3010).—NaOEt–EtOH at 180° converts cholestane-3 : 6-dionedisemicarbazone and chlorogenone disemicarbazone into epimerides, whence digitonin separates cholestan-3(*β*)-ol and tigogenin, respectively, the 3- but not the 6-CO being reduced. R. S. C.

Saponins and sapogenins. XVII. Structure of the side-chain of chlorogenin. K. Ladenburg and C. R. Noller (*J. Amer. Chem. Soc.*, 1941, **63**, 1240—1242).—Me chlorogenoate diacetate (**I**) and NH_3 in EtOH, first at <0° and then at

room temp., give an impure, unstable substance (amorphous platinichloride), which, because of its absorption spectrum, is considered to contain a pyrrole nucleus as in (*A*). The product is basic owing to the accumulation of substituents. (I) reacts also with NH_2Me, but not with NH_2Ph at 160°.



(*A*.)

R. S. C.

Chemical components of the roots of *Decalepis Hamiltonii* (Makali vera). I. Chemical composition of the roots. P. B. R. Murti and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **13, A,** 221—231).—The light petroleum extract (~3%) of the air-dried root is separated by EtOH into sol. and insol. portions. The latter after hydrolysis and careful fractionation is divided into a ketone, m.p. 83°, alcoholic substances belonging to the resinol groups, m.p. 151—165°, a phytosterol mixture, m.p. ~110° (acetates, m.p. 130—160°), and solid and liquid fatty acids. The former yields resinols, m.p. 175—185°, a *compound*, $C_{32}H_{52}O_2$, m.p. 235—236°, and 4 : 2 : 1-$OMe{\cdot}C_6H_3(OH){\cdot}CHO$. The alcoholic extract of the residue gives saponins, tannins, a cryst. resin *acid*, $C_{22}H_{28}O_{10}$, m.p. 245°, an amorphous acid, m.p. ~180°, and inositol. Other solvents do not appear useful as extractives. H. W.

Cerin and friedelin. VI. Surface films of cerin, friedelin, and related substances. N. L. Drake and J. K. Wolfe (*J. Amer. Chem. Soc.*, 1940, **62**, 3018—3021; cf. A., 1939, II, 18).—Pressure–area relations of surface films of friedelin and some of its derivatives show that the CO is at one end of the mol., certainly not in ring c. Similar experiments with cerin and some of its derivatives show that the OH and CO are close together. R. S. C.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Monascin. P. Karrer and A. Geiger (*Helv. Chim. Acta*, 1941, **24**, 289—296).—Monascin (I) readily becomes associated in C_6H_6 and somewhat less readily in $CHBr_3$; it is therefore more probably $C_{20}H_{24}O_5$ or $C_{20}H_{26}O_5$ than $C_{24}H_{30}O_6$. (I), m.p. 141—142°, $[\alpha]_D^{18}$ +571° in EtOH, does not contain S or OMe. One active H is present (Zerevitinov) but the presence of OH is not established since (I) could not be acetylated or benzoylated. (I) contains at least three CMe groups. Ozonisation of (I) in CCl_4 leads to an insol. resinous ozonide which with boiling H_2O gives considerable amounts of MeCHO and AcCHO showing the presence of CHMe: and :CMe·CH:, the latter possibly existing in an isoprene residue. *n*-Hexoic acid is obtained by oxidation of (I) or perhydromonascin with $KMnO_4$ (the p-*bromophenacyl* esters of *n*- and *iso*-hexoic, *dl*-*α*- and *dl*-*β*-methylvaleric acid have m.p. 71°, 77°, 36°, and 38°, respectively). The isolation of AcCHO and the colour of (I) establish the presence of conjugated double linkings. In presence of PtO_2 in AcOH (I) adds 4 H_2, giving the non-cryst. *perhydromonascin*, which does not yield a cryst. *p*-nitro- or dinitro-phenylhydrazone; frequently reaction ceases after addition of 3 H_2 with formation of a cryst. *product*, m.p. 128—129°. Treatment with Zn dust and a little AcOH in C_5H_5N converts (I) into the colourless *dihydromonascin* (II), decomp. >162°. (I) appears to contain a chromophoric system analogous to those of bixin, crocetin, and rhodoxanthin; the groups which yield MeCHO and AcCHO are not here involved since these substances are also obtained by the ozonisation of (II). This unsaturated system is short, probably containing not more than two conjugated double linkings. (I) possibly contains 1 enolic OH whilst at least 2 O are present in CO groups. The remaining O have not been characterised. At least two are probably present as ethers but a lactone group could not be detected in (I) or its reduction products. H. W.

Chemical investigation of Indian lichens. III. Isolation of montagnetol, a new phenolic compound, from *Roccella montagnei*. V. S. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **13, A,** 199—202).—The orcinol fraction from *R. montagnei* contains *montagnetol*, (?) $C_{13}H_{20}O_7$, m.p. 154—156°; its separation is described. H. W.

Nature and constitution of shellac. XV. Shellolic acid and similar acids. P. M. Kirk, P. E. Spoerri, and W. H. Gardner (*J. Amer. Chem. Soc.*, 1941, **63**, 1243—1246; cf. B., 1938, 685).—The EtOH-insol. Pb salts from lac acids yield >3·6% of shellolic acid (I), m.p. 206° (decomp.) [Me_2 ester, m.p. 150°; dihydrazide, m.p. 246° (decomp.) (lit. 243—244°); photomicrographs], homologues, m.p. 166° and 226°, of dihydroshellolic acid (II), an isomeride, m.p. 238°, of (I), and isomerides, m.p. 226° and 245°, of (II). R. S. C.

V.—HETEROCYCLIC.

Derivatives of tetrahydrofurfuryl alcohol. R. D. Kleene and S. Fried (*J. Amer. Chem. Soc.*, 1941, **63**, 1482).—*Tetrahydrofurfuryl H phthalate*, m.p. 175—177°, and *α-naphthylurethane*, m.p. 88—90°, are prepared. R. S. C.

Behaviour of different tocopherols in the colour reaction with nitric acid. P. Karrer and H. Rentschler (*Helv. Chim. Acta*, 1941, **24**, 302—304).—α-Tocopherol and 7 : 8-dimethyltocol give colours of nearly the same intensity when treated with HNO_3 under identical conditions, whereas the colours from 5 : 8- and 5 : 7-dimethyltocol are appreciably less intense. The colorimetric behaviour of β- and γ-tocopherol is in harmony with the hypothesis that they are optically active forms of 5 : 8- and 7 : 8-dimethyltocol, respectively. 5 : 6-*Dihydroxy*-2 : 7 : 8-*trimethylchroman* has m.p. 141°. H. W.

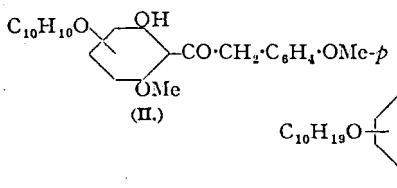
***dl*-5 : 7-Diethyltocol, a further homologue of α-tocopherol.** P. Karrer and R. Schläpfer (*Helv. Chim. Acta*, 1941, **24**, 298—302).—3 : 5 : 1-$C_6H_3Et_2{\cdot}OH$ is converted by $NaNO_2$ and conc. HCl in EtOH at 0° into 4-*nitroso*-3 : 5-*diethylphenol*, m.p. 132°, reduced (H_2–Pt in AcOH–EtOH at 60°) to 4 : 3 : 5 : 1-$NH_2{\cdot}C_6H_2Et_2{\cdot}OH$, which is transformed by H_2SO_4 and $NaNO_2$ into 3 : 5-*diethyl*-p-*benzoquinone*, m.p. 39°. This is reduced to 3 : 5-diethylquinol, m.p. 119°, which is condensed with phytol or phytyl bromide to the viscous, non-cryst. dl-5 : 7-*diethyltocol* (I), characterised as the *allophanate*, m.p. 107°. Physiologically (I) is about as active as 5 : 8- and somewhat less potent than 5 : 7-dimethyltocol. Me groups in the C_6H_6 ring of the tocols are not essential if Et residues take their place. H. W.

Hydrogenation of substituted coumarins. P. L. de Benneville and R. Connor (*J. Amer. Chem. Soc.*, 1940, **62**, 3067—3070).—The following results of hydrogenation are reported. Pressures are 100—200 atm., other conditions as stated. 4 : 7-Dimethylcoumarin gives (Cu chromite; 250°) 4-*γ-hydroxy*-sec.-*butyl*-m-*cresol* (I) (80%), m.p. 73—74° (corr.), b.p. 179—180°/6 mm., or (Raney Ni in C_7H_{14}) 4 : 7-*dimethylhexahydrochroman*, b.p. 121—122°/38 mm. [at 250° 75% with 5% of (?) 4 : 7-dimethyloctahydrochroman (II), b.p. 148—150°/9 mm.; at 205° 44% with 13% of (I), ~19% of (II), and a little H_2-derivative]. 7-Methylcoumarin (modified prep.), m.p. 124—126°, gives (Cu chromite; 250°) 4-*γ-hydroxy*-n-*propyl*-m-*cresol* (76%), m.p. 64·5—65° (corr.), b.p. 156—157°/4 mm. 6-Methylcoumarin (modified prep.), m.p. 72°, gives (Cu chromite; 250°) 3-*γ-hydroxy*-n-*propyl*-p-*cresol* (81%), b.p. 153—154°/3 mm. 6-Hydroxy-4-methylcoumarin (modified prep.), m.p. 250—254°, in C_7H_{14} at 250° gives 6-*hydroxy*-4-*methylhexahydrochroman*, b.p. 149—153°/19 mm. (with Cu chromite 35% or Raney Ni 45%), and other products. 7 : 8-Benzocoumarin at 250° gives (Cu chromite) 2-*γ-hydroxy*-n-*propyl*-1-*naphthol* (III) (31%), m.p. 87—88° (corr.), and *tetrahydro*-7 : 8-*benzochroman* (5%), b.p. 116—120°/4 mm. [with $KMnO_4$ gives only *o*-$C_6H_4(CO_2H)_2$], or (Raney Ni in C_7H_{14}) *decahydro*-7 : 8-*benzochroman* (47%), b.p. 111—113°/5 mm. With Raney Ni in EtOH at 230° 6- (prep. from 4 : 1 : 3-$OH{\cdot}C_6H_3Me{\cdot}[CH_2]_3{\cdot}OH$; method, A., 1940, II, 186), b.p. 111—112°/18 mm., and 7-*methylchroman* (similar prep.), b.p. 141—143°/60 mm., give 72% of 6-, b.p. 100—101°/25 mm., and 7-*methylhexahydrochroman*, b.p. 95—97°/25 mm., respectively. 7 : 8-*Benzochroman*, b.p. 140—142°/5 mm., is prepared from (III), and 4 : 7-*dimethylchroman*, b.p. 135—136°/38 mm., from (I). The course of the hydrogenations is discussed. (Cf. A., 1940, II, 186.) R. S. C.

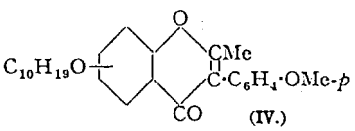
Heterocyclic compounds. XII. Chromones from resacyl- and gallacyl-phenones containing long-chain acyl groups and chemical properties of these hydroxyketones. R. D. Desai and W. S. Waravdekar (*Proc. Indian Acad. Sci.*, 1941, **13, A,** 177—183).—*m*-$C_6H_4(OH)_2$, stearic acid, and anhyd. $ZnCl_2$ at 150° give 4-*stearoylresorcinol* (I), m.p. 89—90° (p-*nitrophenylhydrazone*, m.p. 95—96°), transformed by Ac_2O and anhyd. NaOAc at 175—180° into 7-*acetoxy*-2-*methyl*-3-*hexadecylchromone*, m.p. 82—83°, which is hydrolysed by boiling 5% NaOH to (I). Br in AcOH converts (I) into 6-*bromo*-,

m.p. 98—99°, which could not be further brominated, and HNO_3 (*d* 1·5) in AcOH transforms (**I**) into 6-*nitro*-, m.p. 97—98°, -4-*stearoylresorcinol*. Clemmensen reduction of (**I**) leads to 4-*octadecylresorcinol*, m.p. 83—84°, which does not give a colour with $FeCl_3$ in EtOH. 4-*Palmitoylresorcinol* (**II**), m.p. 89—90° (p-*nitrophenylhydrazone*, m.p. 94—95°; 6-*bromo*-, m.p. 92—93°, and 6-nitro-, m.p. 97—98°, -derivatives), gives 7-*acetoxy*-2-*methyl*-3-*tetradecylchromone*, m.p. 93—94°, hydrolysed by alkali to (**II**). 4-*Hexadecylresorcinol* has m.p. 86—87°. 4-Lauroylresorcinol, m.p. 74° (p-*nitrophenylhydrazone*, m.p. 86—87°), is converted into 6-*bromo*-4-*lauroylresorcinol*, m.p. 84—85°, not affected by heating with alkali or capable of further bromination, and 4-*dodecylresorcinol*, m.p. 137—138°. 1 : 2 : 3-$C_6H_3(OH)_3$ is converted by short heating with stearic acid preferably in presence of $NaHSO_3$ into 4-*stearoylpyrogallol* (**III**), m.p. 80—81° (p-*nitrophenylhydrazone*, m.p. 154—155°; 6-*bromo*-, m.p. 86—87°, and 6-*nitro*-, m.p. 95—96°, -derivatives), converted into 7 : 8-*diacetoxy*-2-*methyl*-3-*hexadecylchromone*, m.p. 92—93°, which is hydrolysed by alkali exclusively to (**III**). 4-*Octadecylpyrogallol*, m.p. 114—115°, does not give a colour with $FeCl_3$ in EtOH. 4-*Palmitoylpyrogallol* (**IV**), m.p. 84—85° (p-*nitrophenylhydrazone*, m.p. 171—172°; 6-*bromo*-, m.p. 87—88°, and 6-*nitro*-, m.p. 92—93°, -derivatives), 7 : 8-*diacetoxy*-2-*methyl*-3-*tetradecylchromone*, m.p. 104—105° [hydrolysed by alkali to (**IV**)], and 4-*hexadecylpyrogallol*, m.p. 115—116°, are described. 4-*Lauroylpyrogallol*, m.p. 74—75° (p-*nitrophenylhydrazone*, m.p. 182—183°), gives a 6-*Br*-derivative, m.p. 80—81°, and 4-*dodecylpyrogallol*, m.p. 170—171°. H. W.

Osage orange pigments. VI. *iso*Flavone nature of osajin. M. L. Wolfrom, J. E. Mahan, P. W. Morgan, and G. F. Johnson. **VII. *iso*Flavone nature of pomiferin.** M. L. Wolfrom and J. E. Mahan (*J. Amer. Chem. Soc.*, 1941, **63**, 1248—1253, 1253—1256; cf. A., 1941, II, 145).—VI. The *iso*flavone structure of osajin (which exists as such in the fruit) is confirmed. Tetrahydro-osajin, Me_2SO_4, and KOH in H_2O–$COMe_2$ give the *Me*$_2$ *ether* (**I**), m.p. 121—121·5°, converted by boiling NaOH–aq. EtOH into HCO_2H and *tetrahydro-osajetin Me*$_2$ *ether* (**II**), m.p. 87° [*oxime, forms*, m.p. 108·5—109·5° and (+H_2O) 88·5—89°]. With boiling KOH–EtOH, (**I**) or (**II**) gives *p*-OMe·C_6H_4·CH_2·CO_2H (**III**) (p-*nitrobenzyl* ester, m.p. 73·5—74·5°). Ac_2O–C_5H_5N at 0° converts (**II**)

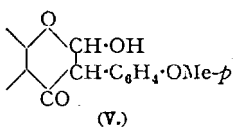


(II.)



(IV.)

into its *acetate*, m.p. 79—80°, but boiling NaOAc–AcOH gives 2-*methyltetrahydro-osajin Me*$_2$ *ether* (**IV**), m.p. 146°, reconverted into (**II**) by NaOH in boiling 50% EtOH. HCO_2Et, Na, and (**II**) in N_2 at 0° give 2-*hydroxyhexahydro-osajin Me*$_2$ *ether* (**V**), m.p. 173° (decomp.), converted into (**II**) by boiling AcOH. Osajin Me_2 ether (**VI**) and NaOH–EtOH give similarly HCO_2H and *osajetin Me*$_2$ *ether* [as (**II**)], m.p. 65—65·5°, which, as above, yields (**III**), 2-*hydroxy*-2 : 3-*dihydro-osajin Me*$_2$ *ether*, m.p. 139—139·5°, and thence (**VI**). The Wilson H_3BO_3 test (A., 1939, II, 528) is diagnostic of OH·C·CO·C:C or OH·C·C(OH):CH.



(V.)

VII. Similar evidence is adduced for pomiferin. *Tetrahydropomiferin Me*$_3$ *ether* (**VII**) [prep. by methylation of tetrahydropomiferin or hydrogenation of pomiferin Me_3 ether (**VIII**)], m.p. 127—128°, and alcoholic alkali give HCO_2H and *tetrahydropomiferitin Me*$_3$ *ether* (**IX**), m.p. 78·5—79·5° (*oxime*, m.p. 133—133·5°), and thence by KOH–EtOH 3 : 4-$(OMe)_2C_6H_3$·CO_2H (**X**) (*phenacyl* ester, m.p. 66·5—67°). HCO_2Et and Na convert (**IX**) into 2-*hydroxyhexahydropomiferin Me*$_3$ *ether*, m.p. 129—130°, which in boiling AcOH gives (**VII**). Alkali similarly converts (**VIII**) into HCO_2H and *pomiferitin Me*$_3$ *ether*, m.p. 64·5—65°, and thence (**X**), 2-*hydroxy*-2 : 3-*dihydropomiferin Me*$_3$ *ether*, m.p. 143—144°, and (**VIII**). R. S. C.

Heterocyclic compounds. XIII. Abnormal alkaline hydrolysis of some 4-*iso*propyl-1 : 2-α-naphthapyrones. S. A. Alt, R. D. Desai, and H. P. Shroff (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 184—187).—α-$C_{10}H_7$·OH and anhyd. $ZnCl_2$ in boiling $Pr^{\beta}CO_2H$ yield 2 : 1-$C_{10}H_6Bu^{\beta}$·OH (**I**), m.p. 87—88° (lit. 77°), transformed by Ac_2O and anhyd. NaOAc at 175—180° into 4-iso*propyl*-1 : 2-α-*naphthapyrone*, m.p. 105°, which is hydrolysed by boiling 5% NaOH to 1 : 2-OH·$C_{10}H_6$·CO_2H. (**I**) is transformed by Br in AcOH into 4-*bromo*-2-iso*butyryl*-1-*naphthol*, m.p. 71°, whence 6-*bromo*-4-iso*propyl*-1 : 2-α-*naphthapyrone*, m.p. 98°, hydrolysed to 1 : 4 : 2-OH·$C_{10}H_5Br$·CO_2H. Gradual addition of AcCl to anhyd. $ZnCl_2$ and (**I**) in $PhNO_2$ leads to 4-*acetyl*-2-iso*butyryl*-1-*naphthol*, m.p. 80°, whence 6-*acetyl*-4-iso*propyl*-1 : 2-α-*naphthapyrone*, m.p. 85°, hydrolysed by alkali to 1 : 4 : 2-OH·$C_{10}H_5$Ac·CO_2H. Alkaline hydrolysis is not therefore an unequivocal method for the identification of coumarins and chromones. If Br in glacial AcOH is added to a coumarin or chromone in the same solvent, the former invariably gives the Br-substituted derivative whereas the latter affords the diperbromide from which the original chromone can be regenerated by aq. H_2SO_3. H. W.

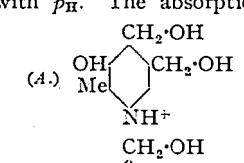
Derivatives of diphenylene oxide. VI. 4-Nitrodiphenylene oxide and its derivatives. S. Yamashiro (*Bull. Chem. Soc. Japan*, 1941, **16**, 61—69).—Diphenylene oxide with HNO_3 (*d* 1·52) in AcOH gives 2- (71%), 3- (**I**) (10%), and 5-*nitrodiphenylene oxide* (**II**) (1%), m.p. 126—126·5°, reduced ($SnCl_2$–conc. HCl–EtOH) to 5-*aminodiphenylene oxide*, m.p. 113·5—114·5° (*Ac* derivative, m.p. 259—260°). 1-Nitrodiphenylene oxide, (**I**), or (**II**) with excess of Br in boiling AcOH gives 6-*bromo*-1-, m.p. 231—232°, 6-*bromo*-3-, m.p. 226—227°, and 6-*bromo*-4-*nitrodiphenylene oxide*, m.p. 189·5—190·5°. (**II**) with HNO_3 (*d* 1·45) at room temp. gives 4 : 6(? 3 : 5)-*dinitrodiphenylene oxide* (**III**), m.p. 241—242°, which did not react with excess of Br in boiling AcOH. (**III**) treated with hot HNO_3 (*d* 1·52) for 0·5 hr. gave 2 : 4 : 6-*trinitro*-, m.p. 207—208°, and 2 : 4 : 6 : 7-*tetranitro-diphenylene oxide*, m.p. 253—254°; the former is converted into the latter by hot HNO_3 (*d* 1·52) in 3 hr. The absorption spectra of these compounds are determined. J. L. D.

2 : 4-Diketo-3 : 3-dialkylpyrrolidines.—See B., 1941, III, 187.

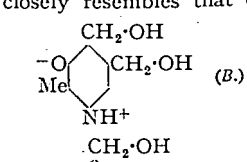
Sulphanilyl-pyrrolidine and -pyrroline. W. E. Cass (*J. Amer. Chem. Soc.*, 1940, **62**, 3255—3256).—*p*-NHAc·C_6H_4·SO_2Cl with pyrrolidine in dioxan at room temp. or pyrroline and C_5H_5N in boiling $COMe_2$ gives N^4-*acetylsulphanilyl-pyrrolidine*, m.p. 179° (corr.), and *-pyrroline*, m.p. 201—202° (corr.), hydrolysed by boiling 12% HCl to *sulphanilyl-pyrrolidine*, m.p. 167·5—168° (corr.), and *-pyrroline*, m.p. 176—177° (corr.), which have little antipneumococcal activity. Other methods of prep. failed. R. S. C.

Preparation and magnetic properties of complex compounds of bivalent chromium.—See A., 1941, I, 344.

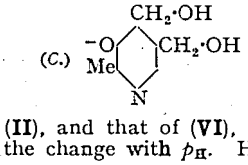
Chemistry of vitamin-B_6. I. Tautomerism. S. A. Harris, T. J. Webb, and K. Folkers. **II. Reactions and derivatives.** S. A. Harris (*J. Amer. Chem. Soc.*, 1940, **62**, 3198—3203, 3203—3205).—I. Vitamin-B_6 (**I**) with boiling MeI–C_6H_6–MeOH gives its *methiodide* (**II**), m.p. 188—189°, which with Ag_2O in H_2O gives N-*methylvitamin*-B_6 *betaine* (**III**), m.p. 196°, also obtained with the *O*-methylvitamin-B_6 (**IV**) from (**I**) by CH_2N_2–MeOH. (**IV**) and MeI at 100° or (**III**) with boiling MeI–C_6H_6 or MeI at 110—115° give *O-methylvitamin-B*$_6$ *methiodide* (**V**), m.p. 124·5—126°. 3-Hydroxypyridine (**VI**) and MeI at 100° give the *methiodide* (**VII**), m.p. 114—116°. 4-*Hydroxy*-3-*methyl*isoquinoline (**VIII**), m.p. 180° (hydrobromide, m.p. 232—233°), is prepared from the 4-OMe-derivative hydrochloride by 48% HBr. The absorption spectra of (**II**) and (**III**) are identical, both changing greatly with p_H. The absorption of (**I**) closely resembles that of



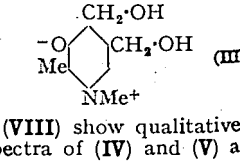
(A.)



(B.)



(C.)



(III.)

(**II**), and that of (**VI**), (**VII**), and (**VIII**) show qualitatively the change with p_H. However, spectra of (**IV**) and (**V**) are

different and independent of p_H. It is concluded that in H_2O (I) shows tautomerism (*A*) ⇌ (*B*) ⇌ (*C*), and that (VI), (VII), and (VIII) behave similarly. Behaviour of (I), (II), (III), and (VII) on electrometric titration supports this view and is closely correlated with changes in absorption spectra. In EtOH, (I) exists mainly (absorption spectrum) in the hydroxypyridine form, although some tautomerism is apparent from the dual effect of CH_2N_2. (II), (III), and (VIII) have little, if any, -B_6 activity.

II. Vitamin-B_6 hydrochloride (IX) and Ac_2O–C_5H_5N, first at room temp. (overnight) and then at 100° (20 min.), give vitamin-B_6 triacetate (X) (*hydrochloride*, m.p. 157°), stable in 0·01N-HCl, slowly hydrolysed by 0·01N-NaOH at 37°. 3-Hydroxy-2-methyl-4 : 5-di(bromomethyl)pyridine hydrobromide with AgOAc–KOAc–AcOH at 100° gives the diacetate (XI) (hydrochloride, m.p. 160—161°) of (I) and with H_2–Pd–$BaCO_3$ gives 3-*hydroxy*-2 : 4 : 5-*trimethylpyridine* (XII), m.p. 178° (*hydrochloride*, m.p. 216°). H_2–PtO_2 reduces (IX) in 95% EtOH to 3-hydroxy-2 : 4-dimethyl-5-hydroxymethylpyridine (XIII) [hydrochloride, m.p. 267—268° (lit. 254°)]. With 1 equiv. of NaOMe in MeOH at 125° or 130°, (IX) gives 3-hydroxy-2-methyl-5-hydroxymethyl-4-methoxymethylpyridine [hydrochloride, m.p. 181° (? or 168°)] (cf. A., 1940, II, 105°). (X) and (XI) are biologically as potent as (I), but (XII) and (XIII) are ineffective. (XIII), but not (XII), is weakly active in promoting growth of, and formation of acid by, *Streptobacterium plantarum*. R. S. C.

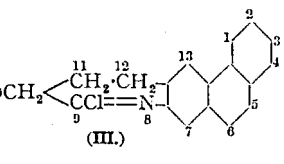
Nitrogen compounds in petroleum distillates. XXI. Isolation and synthesis of 2 : 3 : 4-trimethyl-8-*iso*propylquinoline. XXII. Isolation and synthesis of 2 : 3-dimethyl-4 : 8-diethylquinoline and 2 : 3-dimethyl-4-ethyl-8-*n*-propylquinoline. L. M. Schenck and J. R. Bailey (*J. Amer. Chem. Soc.*, 1941, **63**, 1364—1365, 1365—1367; cf. A., 1941, II, 174).—XXI. —Distillation of fractions previously (A., 1940, II, 357) obtained from Californian petroleum gives 2 : 3 : 4-*trimethyl*-8-iso*propylquinoline*, m.p. 106—107°, b.p. 327°/750 mm. [*picrate*, m.p. 165—166°; *nitrate*, m.p. 143—144° (decomp.); *H sulphate*, m.p. 204—205°], oxidised by $K_2Cr_2O_7$–H_2SO_4 to 2 : 3 : 4-trimethylquinoline-8-carboxylic acid and synthesised from *o*-cumidine (modified prep.) and $CHMeAc_2$.

XXII. Purification, by way of various salts, of fractions previously obtained (A., 1940, II, 24) gives 2 : 3-*dimethyl*-4 : 8-*diethyl*- (I), b.p. 319°/752 mm. (*picrate*, m.p. 174—175°; *H sulphate*, m.p. 170—171°), and 2 : 3-*dimethyl*-4-*ethyl*-8-n-*propyl-quinoline* (II), b.p. 327°/752 mm. [nitrate, m.p. 161° (decomp.); *H sulphate*, m.p. 163—164°]. $K_2Cr_2O_7$–H_2SO_4 oxidises (I) and (II) to 2 : 3-dimethyl-4-ethylquinoline-8-carboxylic acid. Pr^aCO_2H is obtained from (II) by O_3. (I) and (II) are synthesised from $COEt_2$, paraldehyde, and dry HCl with *o*-$C_6H_4Et{\cdot}NH_2$ and *o*-$C_6H_4Pr^a{\cdot}NH_2$, respectively, at 0°. R. S. C.

6-Methyl-5 : 8-quinolinequinone. W. G. Christiansen and M. A. Dolliver (*J. Amer. Chem. Soc.*, 1941, **63**, 1470).—By successive coupling with *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$, reduction by $SnCl_2$, and oxidation by $K_2Cr_2O_7$ 6-methylquinoline gives the 5 : 8-*quinone*, m.p. 167—168°, which gives Craven's test for quinones but has no vitamin-*K* activity. R. S. C.

Preparation and properties of 4-substituted *iso*quinolines. F. W. Bergstrom and J. H. Rodda (*J. Amer. Chem. Soc.*, 1940, **62**, 3030—3032).—4-Bromo*iso*quinoline (I) (prep. by Br in 48% HBr at 180—190°), m.p. 39—40°, and a little Cu and $CuSO_4$ in aq. NH_3 at 250° give 16% of 4-*amino*isoquinoline, m.p. 108° [obtained in 17% yield by use of Cu + $Cu(NO_3)_2$ at 106°]. 4-Cyano*iso*quinoline (II) and boiling 20% NaOH give 98% of quinoline-4-carboxylic acid (III), m.p. 263—265° (*Et* ester, m.p. 47—48°), the *amide*, m.p. 174·5—175·5°, of which is obtained from (II) (64% yield) by H_2O_2–NaOH. In liquid NH_3, KNH_2 (excess) and (III) give an insol. *K* salt, +2NH_3; the mixture than slowly yields H_2 and 1-*amino*isoquinoline-4-*carboxylic acid*, m.p. 249—250° (decomp.), which above the m.p. gives 1-amino*iso*quinoline. With NaOMe–MeOH at 235° or KOBu$^\gamma$–Bu$^\gamma$OH at 180—190° (or 235°), (I) gives ~50% of *iso*quinoline. R. S. C.

Retene field. XII. Synthesis of 10-phenanthr[2, 3-*b*]azepine derivatives by Beckmann rearrangement of a tetrahydrobezretene ketoxime. (Miss) S. A. Cassaday and M. T. Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 1452—1455; cf. A., 1941, II, 175).—γ-3-Retylbutyric acid (prep. from the γ-CO-acid), m.p. 179—180°, and $SnCl_4$ at 110—115° give 8-keto-7-methyl-3-*iso*propyl-8 : 9 : 10 : 11-tetrahydrobenz[*a*]anthracene (5-keto-10-methyl-4′-*iso*propyl-5 : 6 : 7 : 8-tetrahydrobenz-1′ : 2′-1 : 2-anthracene), m.p. 139—140°, the oxime (I), m.p. 202·5—203·5° [*hydrochloride*, m.p. 185—188° (decomp.); *picrate*, m.p. 206·5—207·5°; hydrolysed to the ketone by conc. HCl at 100°], of which with PCl_5 in boiling C_6H_6 gives an additive *product* (II), *X* + 2HCl, m.p. 215—216° (decomp.), of 9-chloro-7-methyl-3-*iso*propyl-11 : 12-dihydro-10-phenanthr[2, 3-*b*]azepine (III). Hydrolysis of (II) by 50% H_2SO_4 at 165—175° gives an additive *product* (IV), *X* + 2HCl, m.p. 259—260° (decomp.), of 7-*methyl*-3-iso*propyl*-11 : 12-*dihydro*-10-*phenanthr*[2, 3-b]*azepin*-9(8)-*one* (V) [as (III) with CO·NH replacing CCl:N]. With PCl_5–C_6H_6, (IV) gives (II) and with conc. HCl at 100° gives γ-2-*amino*-3-*retylbutyric acid hydrochloride*, m.p. 212—213°. (I) and 50% H_2SO_4 at 165—175° (gives a S-compound, m.p. 204—206°), followed by boiling 80% AcOH, gives (V), m.p. 210—211° (*picrate*, m.p. 235—236°). M.p. are corr.


(III.)

R. S. C.

Pyrimidines. Derivatives of pyrimidine-5-carboxylic acid. J. C. Ambelang and T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 1289—1291).—No pyrimidine is obtained from $CN{\cdot}CH(CO_2Et)_2$, $CO(NH_2)_2$ (I), and NaOEt in EtOH at 100°, from the *Na* derivative of $(CN)_2CH{\cdot}CO_2Et$ or the Me ester and (I) or $CS(NH_2)_2$ in EtOH [$CS(NH_2)_2$ gives a small amount of a substance, m.p. 198·5—199·5° (decomp.), containing S and N]. 4-Iminobarbituric acid and (I) at 150—160° give NH_3 and 2 : 6-*diketo*-4-*carbamylimino*-1 : 2 : 3 : 4-*tetrahydropyrimidine*-5-*carboxylamide*, m.p. >300° (*Na* salt), unaffected by boiling HCl and converted by Br–H_2O into 5 : 5-dibromobarbituric acid. $CH_2(CN)_2$ and (I) give only 5% of barbituric acid 4 : 6-di-imide. R. S. C.

Pyrimidines. CLXX. Interaction of chloromethyl ether with pyrimidines. I. (Miss) M. M. Endicott and T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 1286—1289).—Reactions of $CH_2Cl{\cdot}OMe$ (I) in AcOH are due to formation of $OMe{\cdot}CH_2{\cdot}OAc$ (cf. Vavon *et al.*, A., 1937, II, 372). 6-Keto-2-ethylthiol-4-methylpyrimidine (II) and (I) in AcOH give the dimorphic *hydrochloride*, +H_2O (lost at 100°/vac.), m.p. 170·5—172°, which at 190—195° gives HCl, EtSH, 4-methyluracil (III), and 6-keto-2-thio-4-methylpyrimidine, decomp. >285°. 2 : 6-Dichloro-4-methylpyrimidine and (I) in AcOH at room temp. give HCl, 2-*chloro*-6-*keto*-4-*methylpyrimidine hydrochloride* (IV), decomp. >275°, and a "*polymeride*" (V), unchanged at <340°, of 4-methyl-5-hydroxymethyluracil; in boiling AcOH 98% of (V) is formed. In boiling abs. EtOH, (IV) gives 6-*keto*-2-*ethoxy*-4-*methylpyrimidine hydrochloride*, decomp. 312—314°, which with Na_2CO_3 (1 equiv.) yields the known base. HI and red P in AcOH reduce (V) to (4 : 5-dimethyluracil (VI) and *di*-(2 : 6-*diketo*-4-*methyl*-5-*pyrimidyl*)*methane* (VII), unchanged at 340° [also obtained from (V) by conc. HCl]. Boiling (III) with (I) or $OMe{\cdot}CH_2{\cdot}OAc$ in AcOH gives 4-*methyl*-5-*acetoxymethyluracil* (VIII), shrivels at 233°, decomp. 320° (gas), and (VII). Condensation of (III) and (VIII) by dry HCl in boiling AcOH gives (VII). Reduction of (VIII) by red P–HI–AcOH gives (VII) and (VI). R. S. C.

Applications of *X*-ray methods in the examination of organic crystals.—See A., 1941, I, 325.

Preparation of derivatives of *iso*propylbenzene and of 7 : 7′-dichloro-4 : 4′-di*iso*propylthioindigotin. P. Kirjakka (*Suomen Kem.*, 1940, **13, B**, 22).—Chlorination of $PhPr^\beta$ gives *p*-$C_6H_4Pr^\beta Cl$, which with 7% oleum affords 3 : 6 : 1-$C_6H_3Pr^\beta Cl{\cdot}SO_3H$ [Ba salt, a syrup; chloride (I), b.p. 172—174°/22 mm.; amide, m.p. 143—143·5°]. (I) gives 3 : 6 : 1-$C_6H_3Pr^\beta Cl{\cdot}SH$, b.p. 134·5—135·5°/22 mm., and thence the thiolacetic acid, m.p. 103—104°, and finally 7 : 7′-dichloro-4 : 4′-di*iso*propylthioindigotin (dyes cotton and wool from a $Na_2S_2O_4$-vat red-violet). J. L. D.

Triazines.—See B., 1941, II, 256.

Preparation of adenosine triphosphate. S. E. Kerr (*J. Biol. Chem.*, 1941, **139**, 121—130).—Ba_2 adenosine triphosphate is prepared from muscle by pptn. of the neutralised $CCl_3{\cdot}CO_2H$ extract with AcOH (to 0·2%) and 20% $Hg(OAc)_2$, treatment of the ppt. with H_2S, removal of Fe by H_2S in alkaline solution, and addition of $Ba(OAc)_2$. Repeated pptn. of the Ba_2 salt with EtOH from dil. HCl solution yields the Ba salt.

The free acid yields with dil. HNO_3, EtOH, and $AgNO_3$, the Ag_3, and with excess of AgOAc, the Ag_4 salt. The Na salt with $Hg(OAc)_2$ and EtOH yields a sol. "complex." A. Li.

Preparation of muscle adenylic acid. S. E. Kerr (*J. Biol. Chem.*, 1941, **139**, 131—134).—The prep. of adenylic acid (I) by hydrolysis [$Ba(OH)_2$] of adenosine triphosphate is described. Hydrolysis (N-HCl at 100°) of (I) converts 11% of its P into inorg. P in 1 hr. A. Li.

Mercuri-derivatives of ureides.—See B., 1941, III, 218.

Formation of copper phthalocyanine. H. Z. Lecher, H. T. Lacey, and H. P. Orem (*J. Amer. Chem. Soc.*, 1941, **63**, 1326—1330).—*o*-$C_6H_4(CN)_2$ (I) does not react with pure Cu or Cu^I halides in boiling C_5H_5N in absence of air. O_2 oxidises Cu^I halides in C_5H_5N yielding complexes of Cu^{II} halides with C_5H_5N, CuO (in colloidal solution), and possibly Cu^{II} oxyhalides. O_2 also oxidises Cu powder in boiling C_5H_5N. Small amounts of these products or air initiate formation of Cu phthalocyanine (II) from (I) and pure Cu^I halides. It is concluded that reaction proceeds by formation of $\{Cu[o\text{-}C_6H_4(CN)_2\}^{++}X^-_2$, which is reduced by the Cu^I compound to (II) and CuX_2; the CuX_2 liberated then continues the process. $CuBr_2,2C_5H_5N$ is described. $CuI_2,2C_5H_5N$ is unstable, liberating I and C_5H_5N when dried. R. S. C.

Chemiluminescence of luminol catalysed by iron complex salts of chlorophyll derivatives. E. Schneider (*J. Amer. Chem. Soc.*, 1941, **63**, 1477—1478).—Fe chlorin-e_6, Fe phæophorbide-*a*, and Fe bacteriochlorin-e_6 catalyse the chemiluminescence of luminol, Cu chlorin-e_6, Cu deuteroporphyrin, and sulphonated Cu phthalocyanine do so weakly, and chlorophyllin very weakly. Phæophorbide, chlorin-e_6, [deuteroporphyrin, and coproporphyrin do not. Strong luminescence is dependent on co-ordination of Fe with four pyrrole N. R. S. C.

Invert soaps. Quaternary morpholinium salts. M. E. McGrcal and J. B. Niederl (*J. Amer. Chem. Soc.*, 1941, **63**, 1476).—4-*Ethyl*-4-n-*dodecyl*-, m.p. 201°, *-tetradecyl*-, m.p. 203°, and *-hexadecyl*-, m.p. 207°, 4-*β-hydroxyethyl*-4-n-*dodecyl*-, m.p. 92°, *-tetradecyl*-, m.p. 95°, and *-hexadecyl*-, m.p. 97°, *-morpholinium bromide* are prepared from ethyl- or β-hydroxyethyl-morpholine, respectively, by RCOCl in boiling PhMe. R. S. C.

αβ-Unsaturated amino-ketones. α- and β-Morpholinobenzylideneacetophenones. N. H. Cromwell (*J. Amer. Chem. Soc.*, 1940, **62**, 2897—2900; cf. A., 1940, II, 310).—CHPhBr·CHBr·COPh and morpholine (I) (excess) in abs. EtOH at room temp. or in boiling C_6H_6 give much *αβ-morpholino-β-phenylpropiophenone* (II), *forms*, m.p. 173—175° (decomp.) and 154—156° (decomp.) (hydrolysed to PhCHO, ω-morpholinoacetophenone, and traces of $CH_2Ph·CO·COPh$), and a small amount of *α-morpholinocinnamoylbenzene* ["*α-morpholinobenzylideneacetophenone*"] (III), m.p. 94—96° [hydrolysed to $CH_2Ph·CO·COPh$ (77%)]. CHPh:CBr·COPh and (I) in Et_2O at −5° give *α-bromo-α-morpholino-β-phenylpropiophenone*, m.p. 138—139° (decomp.; block) [with alcoholic (not aq.) $AgNO_3$ gives AgBr], which slowly reacts with more (I) giving approx. equal amounts of (II) and (III), but with NaOEt in boiling EtOH gives 96% of (II). Reaction mechanisms are proposed. Boiling CH_2Bz_2, (I), and a drop of conc. HCl give *β-morpholinocinnamoylbenzene* ["*β-morpholinobenzylideneacetophenone*"] (IV), m.p. 96—97° (unstable hydrochloride), hydrolysed by 15% H_2SO_4 at room temp. to CH_2Bz_2. Attempts to prepare (II) from (III) or (IV) failed. R. S. C.

3-Methylthiazolone-2-*p*-aminobenzenesulphonimide. M. Hartmann and J. Druey (*Helv. Chim. Acta*, 1941, **24**, 536—538).—The product, m.p. 270°, of the methylation of 2-*p*-acetamidobenzenesulphonamidothiazole with Me_2SO_4 and NaOH is 3-*methylthiazolone*-2-p-*acetamidobenzenesulphonimide*, since it is identical with the product derived from 3-methylthiazolone-2-imide and *p*-$NHAc·C_6H_4·SO_2Cl$ in C_5H_5N. It is readily hydrolysed by acids to 3-*methylthiazolone*-2-p-*aminobenzenesulphonimide*, m.p. 245—246°. 2-Methylaminothiazole and *p*-$NO_2·C_6H_4·SO_2Cl$ in dry C_5H_5N yield 2-p-*nitrobenzenesulphonmethylamidothiazole* or 3-p-*nitrobenzenesulphonylthiazolone*-2-*methylimide*, m.p. 108—109°, reduced to the corresponding NH_2-compound, m.p. 109—110°. H. W.

Sulphanilamides.—See B., 1941, III, 216.

1-Chlorothiolbenzthiazole.—See B., 1941, II, 255.

Benzthiazyl 1-thiomethylene esters.—See B., 1941, II, 283.

Furoyl benzthiazyl sulphide.—See B., 1941, II, 284.

Synthesis of *dl*-anolobine *O*-methyl ether (*dl*-5 : 6-methylenedioxy-2-methoxynoraporphine). T. R. Govindachari (*Current Sci.*, 1941, **10**, 76—77).—4-Nitro-3-aldehydophenyl carbonate with hippuric acid and Ac_2O gives the *azlactone*, m.p. 162°, of 2-nitro-5-hydroxybenzaldehyde, which with EtOH–HCl (pressure) at 100° affords 2-*nitro-5-hydroxyphenylpyruvic acid*, m.p. 194°, oxidised (H_2O_2) to 2-*nitro-5-hydroxyphenylacetic acid*, m.p. 199° [*CH_2Ph ether* (I), m.p. 165°]. The acid chloride of (I) with homopiperonylamine (II) gives 2-*nitro-5-benzyloxyphenylacethomopiperonylamide*, m.p. 145—146°, converted by PCl_5 in $CHCl_3$ at room temp. in 7 days into 6 : 7-methylenedioxy-1-(2′-nitro-5′-benzyloxy)benzyl-3 : 4-dihydro*iso*quinoline, reduced (Zn–HCl at 100°) to 6 : 7-methylenedioxy-1-(2′-amino-5′-benzyloxy)benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (*picrate*, m.p. 159°), which is very unstable. With 2-nitro-5-methoxyphenylacetic acid (II) gives 2-*nitro-5-methoxyphenylacethomopiperonylamide*, m.p. 182—183°, converted by PCl_5–$CHCl_3$ at room temp. in 2 days into 6 : 7-*methylenedioxy*-1-(2′-*nitro*-5′-*methoxy*)*benzyl*-3 : 4-*dihydro*isoquinoline, m.p. 166—167° (*picrate*, m.p. 218°), reduced to 6 : 7-methylenedioxy-1-(2′-amino-5′-methoxy)benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (*hydrobromide*, m.p. 244°), which when diazotised and boiled with MeOH gives *dl*-5 : 6-methylenedioxy-2-methoxynoraporphine (*hydrochloride*, m.p. 305°; *hydrochloride* $+H_2O$, m.p. 278°). J. L. D.

Alkaloids of *Fritillaria Roylei*. II. Isolation of peiminine. Y. F. Chi, Y. S. Kao, and K. J. Chang (*J. Amer. Chem. Soc.*, 1940, **62**, 2896—2897).—The formula of peimine, $C_{26}H_{43}O_3N$ (A., 1936, 1131), is confirmed by analysis of the *hydriodide*, m.p. 282—283°, *nitrate*, m.p. 268—269°, and *methochloride platinichloride*, $(B,MeCl)_2PtCl_4$, softens at 230°, m.p. 240° (decomp.). Peiminine (verticilline) (Chou *et al.*, A., 1932, 1178; Fukuda, A., 1930, 227) is $C_{26}H_{43}O_2N$, sinters at 140°, melts at 147—148°, resolidifies at 157°, remelts at 212—213°, and after drying at 110°/vac., m.p. 212—213°. R. S. C.

Veratrine alkaloids. VIII. Selenium dehydrogenation of cevine. L. C. Craig and W. A. Jacobs. **IX. Nature of the hydrocarbons from the dehydrogenation of cevine.** L. C. Craig, W. A. Jacobs, and G. I. Lavin. **X. Structure of cevanthridine.** L. C. Craig and W. A. Jacobs (*J. Biol. Chem.*, 1941, **139**, 263—275, 277—291, 293—299).—VIII. From the products of dehydrogenation (Se) of cevine at 345° by chromatographic analysis and distillation the following are obtained: β-picoline, 5-methyl-2-ethylpyridine (I), 4 : 5-benzhydrindene, cevanthrol, cevanthridine, compounds C_8H_9ON, $C_{17}H_{16}$ (II), $C_{18}H_{18}$, and $C_{26}H_{25}N$ (previously said to be $C_{25}H_{25}N$) [*methiodide*, m.p. ~295° (decomp.)] (A., 1939, II, 459), base $C_9H_{13}N$ (picrate, m.p. 150—151°) (A., 1938, II, 422), *5-methyl-2-hydroxyethylpyridine*, b.p. 225—229° [which gives on oxidation ($KMnO_4$) the same products as (I)], and *compounds* $C_{19}H_{20}$, m.p. 185—188°, $C_{24}H_{30}$, m.p. 108—110°, $C_{23}H_{24}O$, m.p. 181—187°, and $C_{20}H_{19}N$, m.p. 233—235° (*methiodide*, decomp. 285—290°).

IX. Spectroscopic and other evidence shows that the hydrocarbons produced in the dehydrogenation of cevine may be derivatives of *cyclo*penteno-phenanthrene or -fluorene. Perinaphthenone with Se at 340° yields perinaphthane, and with MgMeI yields a *compound*, $C_{14}H_{10}O$, m.p. 87—88°, and *methylperinaphthene*, m.p. 63—65°, converted by Se at 340° into *methylperinaphthane*, b.p. up to 140°/1 mm.

X. Cevanthridine, $C_{25}H_{27}N$ (cf. Blount, A., 1935, 505) (methiodide, m.p. 268—270°), is hydrogenated (PtO_2) to *tetrahydrocevanthridine*, m.p. 158—159° [*hydrochloride*, decomp. ~280—295° (sintering); *Ac*, m.p. 206—207°, and p-*bromobenzoyl* derivative, m.p. 107—113°], which has an ultra-violet absorption spectrum resembling that of (II). A. Li.

VI.—ORGANO-METALLIC COMPOUNDS.

Preparation of phenylarsenoxides. II. Derivatives of amino- and hydroxy-phenylarsenoxides. III. Derivatives of carboxy- and sulpho-phenylarsenoxides. G. O. Doak, H. Eagle, and H. G. Steinman. G. O. Doak, H. G. Steinman, and H. Eagle (*J. Amer. Chem. Soc.*, 1940, **62**, 3010—3011, 3012—3013; cf. A., 1940, II, 111).—II. The following are prepared. p-*Arsino-dimethylaniline*, *-ethylaniline*, *-benzonitrile* (*Na* salt, $+H_2O$), *-benzylamine*, decomp. >300° (from the *Ac* derivative by HCl), and -p′-*aminobenzamide*. *Acet*-p-*arsinoanilide*, m.p. 208—209°. *Na* p-*acetoxyphenylarsinate*. *Acet*-p-*aminobenzylamide*, m.p. 85—86° (from the NO_2-amide by

H_2–Raney Ni in EtOH). p-*Arsenoxido-dimethylaniline*, *-benzylamine* (*Ac* derivative, m.p. 224—226°; corresponding *dichloride* is hydrolysed by NaOH, but not by $NaHCO_3$), and *-acetophenoneoxime*. m-*Arsenoxidoacetanilide*, m.p. 139—140°. p-*Aminobenz*-p′-*arsenoxidoanilide* (*Ac* derivative). p-*Acetoxyphenylarsenoxide*. *p*-$AsO_3H_2{\cdot}C_6H_4{\cdot}[CH_2]_2{\cdot}OH$.

III. Condensation of the appropriate amine or ester with the arsine-benzoyl or -sulphonyl chloride dichloride, alone or in C_5H_5N, gives p-*arsenoxidobenz-dimethylamide*, *-diethylamide*, *-benzylamide*, -p′-*acetamidoanilide*, and -2′-*pyridylamide*, p-*arsenoxidobenzenesulphon-methylamide*, *-ethylamide*, *-β-hydroxyethylamide*, *-dimethylamide*, $+H_2O$, *-diethylamide*, $+H_2O$, and -p′-*carbamylanilide*, $+H_2O$, *γ*-p-*arsenoxidophenylbutyramide*, *Et* m-*arsenoxidobenzoate*, o-, $+H_2O$, and p-*arsenoxidobenzamide*, $+H_2O$, p-*arsenoxido-phenylacetamide*, *-cinnamamide*, *-benzanilide*, $+H_2O$, and *-hippuric acid*, and o-*arsenoxidobenzenesulphonamide*, $+H_2O$. Reduction of the corresponding arsinic acids gives p-*arsenoxido-phenylacetic acid*, *-benzenesulphon-2′-pyridylamide* and -2′-*thiazolylamide*, *-phenoxyacetic acid* (*Me* ester, decomp. when kept at −25°; *amide*, $+H_2O$), *-succinanilic acid* (*amide*), *-cinnamic acid*, $+H_2O$, *-benzenesulphonamide*, $+H_2O$, and *-benzamide*, *β*-p-*arsenoxidophenylpropionic* and *γ*-p-*arsenoxidophenylbutyric azid*. The Bart or Bart–Scheller reaction gives *γ*-p-*arsinophenyl*-n-*butyric acid*, m.p. 125·5—126·5°, p-*arsino-phenyl Me sulphide* (converted into the sulphone by 30% H_2O_2), *-benzenesulphon-2′-pyridylamide* and -2′-*thiazolylamide*, *-phenylacetic acid* (*Mg* salt, m.p. 190—192°), and *-cinnamic acid* (reduced by H_2–Raney Ni to *β*-p-*arsinophenylpropionic acid*). R. S. C.

4-Amino-2-hydroxyphenylarsine oxide and related oxides. C. K. Banks and C. S. Hamilton (*J. Amer. Chem. Soc.*, 1940, **62**, 3142—3144).—*m*-$OH{\cdot}C_6H_4{\cdot}NH{\cdot}CO_2Et$ and 87% H_3AsO_4 at 100° give 4 : 2 : 1-$CO_2Et{\cdot}NH{\cdot}C_6H_3(OH){\cdot}AsO_3H_2$ (**I**), m.p. 231—232° (corr.) (lit. 214°). With boiling 3N-NaOH, (**I**) gives 4 : 2 : 1-$NH_2{\cdot}C_6H_3(OH){\cdot}AsO_3H_2$ (**II**), m.p. 184° (lit. 175°). With 2N-NaOH–Me_2SO_4, (**I**) gives 4 : 2 : 1-$CO_2Et{\cdot}NH{\cdot}C_6H_3(OMe){\cdot}AsO_3H_2$, $+2H_2O$, m.p. ~110°, and with PCl_3 in Et_2O at 0°, followed by aq. NH_3, gives 4 : 2 : 1-$CO_2Et{\cdot}NH{\cdot}C_6H_3(OMe){\cdot}AsO$, m.p. 241° (lit. 159°). 4-*Carbo*-n-*propoxy*-, m.p. 209°, and 4-*carbobenzyloxy-amino*-2-*hydroxyphenylarsine oxide*, m.p. 224°, are similarly prepared. Reduction of (**II**) usually causes removal of As, but SO_2 and KI (0·5—2 g. per l.) in 2—6N-H_2SO_4 at <40° gives 4-*amino*-2-*hydroxyphenylarsine oxide*, m.p. >300° [*sulphate*, B,H_2SO_4, m.p. >225° (decomp.); *Na* salt, m.p. >250°]. 4-*Amino*-2-*β-hydroxy-ethoxy*-, $+H_2O$, m.p. ~100°, and -n-*propoxy*-, $+H_2O$, m.p. ~90°, 4-*carbethoxyamino*-2-*β-hydroxy-ethoxy*-, m.p. 222°, and -n-*propoxy*-, m.p. 175°, 4-*carbobenzyloxyamino*-2-*β-hydroxyethoxy*-, m.p. >250°, and 4-*carbethoxyamino*-2-*methoxy*-, m.p. 147°, *-phenylarsine oxide* are also prepared. R. S. C.

Synthesis of lipophilic chemotherapeutics. IV. *N*-Acylated arsanilic acids. L. Haskelberg and F. Bergmann (*J.S.C.I.*, 1941, **60**, 166—168; cf. A., 1940, II, 262).—Atoxyl and RCOCl in boiling C_6H_6 or PhMe at 100° give p-*dichloroacet*- (**I**), *-trichloroacet*-, *-trichloroacryl*-, *-Δ⁴-undecenoyl*-, *-undecoyl*-, *-ακ-dibromoundecoyl*-, -3′ : 4′ : 5′ : 6′-*tetrachloro*-2′-*carboxybenz*- [from $C_6Cl_4(CO)_2O$ in aq. dioxan], *-adipyl*-, and -isophthalyl-, m.p. >360°, *-amidophenylarsinic acid*. (**I**) shows some trypanocidal activity. *Undecoyl chloride* (prep. by $SOCl_2$) has b.p. 90°/1 mm. H. B.

Preparation of germanium tetraphenyl. D. E. Worrall (*J. Amer. Chem. Soc.*, 1940, **62**, 3267).—MgPhBr and $GeCl_4$ in boiling PhMe give good yields of $GePh_4$, m.p. 225—226° (cf. lit.). R. S. C.

Relative reactivities of organometallic compounds. XXXVI. Reversible metal–metal interconversions involving lithium and magnesium. XXXVII. Reversible halogen–metal interconversion reactions. XXXVIII. Catalytic effect of organolithium compounds in interconversion reactions. H. Gilman and R. G. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 1439—1441, 1441—1443, 1443—1447; cf. A., 1941, II, 178).—XXXVI. Reversibility of the reactions, (*a*) $2LiR + HgR'_2 \rightleftharpoons HgR_2 + 2LiR'$, (*b*) $2MgRX + HgR'_2 \rightleftharpoons HgR_2 + 2MgR'X$, and (*c*) $MgR_2 + 2LiR' \rightleftharpoons MgR'_2 + 2LiR$, in Et_2O is demonstrated. Examples are (*a*) and (*b*) Ph–p-tolyl; (*c*) Ph–Pr$^\beta$ (presence of LiPr$^\beta$ proved by addition of $CH_2{:}CPh_2$ and then of CO_2 to give $CPh_2Bu^\beta{\cdot}CO_2H$; presence of LiPh proved by addition of *p*-$OMe{\cdot}C_6H_4{\cdot}CN$ and subsequent hydrolysis to give *p*-$COPh{\cdot}C_6H_4{\cdot}OMe$). In reaction (*a*) with Bu$^\beta$–*p*-tolyl, equilibrium is displaced to give almost entirely LiPh + $HgBu^a_2$; the $HgBu^a_2$ reacts with LiBr present to give $HgBu^aBr$.

XXXVII. The reaction, LiR + R′Hal $\rightleftharpoons$ LiR′ + RHal, is reversible if R and R′ are both aryl (Ph–*p*-tolyl) or alkyl (Et–Bu^a), but not if R = Alkyl (Bu^a) and R′ = aryl (Ph). Possible applications are discussed.

XXXVIII. Small amounts of LiR catalyse the reversible reaction, $HgR_2 + 2R'I \rightleftharpoons HgR'_2 + 2RI$, intermediate steps being $HgR_2 + 2LiR' \rightleftharpoons HgR'_2 + 2LiR$ and $2R'I + 2LiR \rightleftharpoons 2RI + 2LiR'$. $Hg(C_6H_4Br\text{-}p)_2$ and $LiBu^a$ give $LiC_6H_4Br\text{-}p$ (and thence $p\text{-}C_6H_4Br{\cdot}CO_2H$) and then $p\text{-}C_6H_4Br$ [and thence $p\text{-}C_6H_4(CO_2H)_2$]. Competitive interaction of 1 equiv. each of $o\text{-}C_6H_4Br{\cdot}OMe$ (**I**), $HgPh_2$, and $LiBu^a$ gives consecutively and very rapidly the reactions, $HgPh_2 + 2LiBu^a \rightarrow HgBu^a_2 + 2LiPh$, $LiPh + (I) \rightarrow PhBr + o\text{-}LiC_6H_4{\cdot}OMe$ (gives $o\text{-}OMe{\cdot}C_6H_4{\cdot}CO_2H$). When $o\text{-}C_6H_4I{\cdot}OMe$ is used in the last-named reaction, carboxylation after 0·5 min. gives the same products as with (**I**) but after 1 min. $HgPh_2$ is re-formed owing to the LiR-catalysed interaction of PhI and $HgBu^a_2$. When (*a*) $p\text{-}C_6H_4MeI$ and $HgPh_2$ or (*b*) PhI and $Hg(C_6H_4Me\text{-}p)_2$ interact in presence of a little LiPh, $HgPh_2$ and $Hg(C_6H_4Me\text{-}p)_2$ are formed. The scope of the reactions is discussed. R. S. C.

Relative reactivities of organometallic compounds. XXXIV. Organometallic radicals. H. Gilman and F. W. Moore (*J. Amer. Chem. Soc.*, 1940, **62**, 3206—3208; cf. A., 1940, II, 385).—The relative ease of cleavage of organo-metallic compounds depends on the nature of the metal, org. radical, and reagent. $PbPh_4$ and $LiBu^a$ give fairly rapidly $PbBu^a_4$ and LiPh (identified by conversion into BzOH), the reaction being favoured by the solvent in the order, $Et_2O > C_6H_6 >$ light petroleum. $PbPh_4$ does not react appreciably with $NaCH_2Ph$, NaPh, LiPh, or $MgBu^aBr$. The rate of reaction with $LiBu^a$ increases in the order, $PbPh_4 < PbPh_3 < Pb(C_6H_4Me\text{-}p)_3$ and $PbPh_4 < PbPh_2(C_6H_4Me\text{-}p)_2$ (preferential removal of tolyl). R. S. C.

Organic selenium compounds. Nitration of phenyl alkyl selenides and reduction [of the products] to amines. D. G. Foster (*J. Amer. Chem. Soc.*, 1941, **63**, 1361—1362).—HNO_3 fails to nitrate PhSeAlk owing to depletion of the acid by formation of $SePhR(OH){\cdot}NO_3$. *m*-Nitration is effected by evaporating PhSeAlk in conc. HNO_3 at 50°, dissolving the product in fuming HNO_3, adding H_2SO_4 during 1 hr., and heating at 100° for 1 hr. The products are usually isolated as dichloride by adding HCl to the mixture. Thus are obtained m-*nitrophenyl-methyl*-, m.p. 122° [corresponding *nitrate* (**I**), m.p. 111°, and *dibromide* (**II**), m.p. 107°], *-ethyl*-, m.p. 92—93° (corresponding *nitrate*, m.p. 93—94°), -n-*propyl*-, m.p. 103—104°, *-n-butyl*-, m.p. 100°, -n-*amyl*-, m.p. 71—73°, -n-*hexyl*-, m.p. 57°, and -n-*heptyl*-, m.p. 65°, *-selenonium dichloride*. Hydrogenation (Raney Ni; 30—40°) of the appropriate dichloride in H_2O (solution adjusted to p_H 8) gives m-*aminophenyl Me*, b.p. 128°/4 mm., *Et*, b.p. 129°/4 mm., *Pr^a*, b.p. 137°/3 mm., *Bu^a*, b.p. 154°/4 mm., n-*amyl*, b.p. 176°/7 mm., n-*hexyl*, b.p. 174°/4 mm., and n-*heptyl selenide*, b.p. 173°/4 mm. $PhSeO_2H$ is nitrated (as above) and reduced by N_2H_4,H_2SO_4 in aq. NaOH to give *di*-m-*nitrophenyl selenide* (**III**) (95%), m.p. 81°, hydrogenated (Raney Ni; 30—40 lb.; EtOH) to *m*-$NH_2{\cdot}C_6H_4{\cdot}SeH$, m.p. 58° (cryst. *hydrochloride*). Orientation of the products is proved by pyrolysis (120—130°) of (**II**) to *m*-$NO_2{\cdot}C_6H_4{\cdot}SeBr$, hydrolysed by boiling H_2O to a mixture of (**III**) and *m*-$NO_2{\cdot}C_6H_4{\cdot}SeO_2H$ (**IV**), whence pure (**IV**), m.p. 156°, is obtained by conc. HNO_3. Aq. K_2CO_3 converts (**I**) into m-*nitrophenylmethylselenonium dihydroxide*, m.p. 118°. R. S. C.

Organic compounds of silicon. I. Synthesis of silicon tetrabenzyl and tetraphenyl. Z. Manulkin and F. Jakubova (*J. Gen. Chem. Russ.*, 1940, **10**, 1300—1302).—$SiCl_4$ or Na_2SiF_6 and $ClH_2Ph{\cdot}MgCl$ or MgPhCl in Et_2O (4 hr. at the b.p.) give $Si(CH_2Ph)_4$ or $SiPh_4$, both in ~50% yield. R. T.

VII.—PROTEINS.

Proteins. W. T. Astbury (*Chem. and Ind.*, 1941, 491—497; cf. A., 1940, I, 199; II, 199).—The structure of the *α*-forms of proteins is considered, with special reference to keratin and myosin. The *β*-configuration of this group may be represented by a flat grid. The *α*-configuration can be obtained from it by throwing the main chains into a series of regular folds. It is possible to make a fold of the dimensions

required to keep the *d* const., and it is found that this is the shortest fold that leaves the side-chains alternately on one side and the other. The side-chains are close-packed. Keratin and myosin, with different constitutions, have essentially the same mol. pattern, but side-chains can be interchanged if they are of a similar type, thus giving rise to the different constitutions. The structure of corpuscular proteins is also considered. A. J. M.

Hydrolysis of proteins at high temperatures and pressures. I. K. Nakajima and M. Ikeda (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 295—299).—The hydrolysis of soya-bean protein (**I**), caseinogen (**II**), and gelatin (**III**) by H_2O at 140—195°/38—185 atm. for 4—5 hr., and the amounts of sol., NH_2-, and NH_3-N are determined. At 170°/110 atm. (**I**) yields albuminose and peptone-like substances. A pigment of the melanin type is pptd. from the hydrolysate at p_H 2. This is completely hydrolysed by 20% HCl, and proline, leucine, *iso*leucine, phenylalanine, arginine, and aspartic, glutamic, and hydroxyglutamic acid are present in the hydrolysate. The amounts of NH_3-, humin-, monoamino- and diamino-acid-N in the latter are given. (**II**) and (**III**) behave similarly on hydrolysis at high temp. and pressures and analogous data for the hydrolysates and pigments are given. J. N. A.

Magnetic studies of ferrihæmoglobin reactions. II. Equilibria and compounds with azide ion, ammonia, and ethyl alcohol. C. D. Coryell and F. Stitt (*J. Amer. Chem. Soc.*, 1940, **62**, 2942—2951; cf. A., 1937, I, 293).—Ferrihæmoglobin (**I**) forms an azide (**II**) with N^{III} ions, and NH_3-(**I**) hydroxide (**III**) with aq. NH_3. EtOH forms additive compounds with (**I**) and with the hydroxide of (**I**). The influences of these and of MeOH and Pr^{a}OH on the magnetic properties of (**I**) have been studied. Pr^{a}OH causes denaturation. (**II**) and (**III**) contain essentially covalent linkages, whilst the EtOH compounds are essentially ionic. W. R. A.

Determination of the hydroxy-amino-acids of insulin. B. H. Nicolet and L. A. Shinn (*J. Amer. Chem. Soc.*, 1941, **63**, 1486).—Determination of the products obtained from hydroxy-amino-acids (*A*) by HIO_4 is used to determine the threonine, serine, and total (*A*) from insulin. The mol. contains 8 threonine, 12 serine, and 6 other hydroxy-amino-acid residues. R. S. C.

VIII.—ANALYSIS.

Device for continuous liquid–liquid extraction. Determination of morphine.—See A., 1941, I, 350.

Micro-determination of mol.-wt. of dark coloured organic materials.—See A., 1941, I, 307.

Steam-distillation of small quantities of volatile oils lighter than water. F. M. Biffen (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 422—423).—A graduated tube, open at both ends, is inserted in the neck of a separating funnel containing sufficient H_2O to cover the lower end of the tube. The condenser is attached by an adaptor to the top of the tube, and the distillation carried out in the usual way. All the oil accumulates in the graduated tube and its vol. can be read accurately and easily at any point in the distillation. J. D. R.

Apparatus for the absorption or gravimetric determination of constituents of a gas mixture.—See A., 1941, I, 307.

Manometric gas analysis apparatus.—See A., 1941, I, 307.

Apparatus for volumetric gas analysis.—See A., 1941, I, 307.

Identification of sulphonic acids. E. Chambers and G. W. Watt (*J. Org. Chem.*, 1941, **6**, 376—383).—The action of CH_2PhCl on $CS(NH_2)_2$ in boiling 95% EtOH gives an almost quant. yield of *S*-benzylthiuronium chloride (**I**); the variety of low m.p. (140—145°) is converted into that of high m.p. (174°) by crystallisation from H_2O. *Thiuronium* derivatives of the following -sulphonic acids are obtained by the interaction of (**I**) with neutral, alkali salt solutions of the acids and crystallisation of the products from 50% EtOH, identical compounds being obtained from both varieties of (**I**): *ethyl*-, m.p. 114·7°; *thymol*-, m.p. 212·4°; d-*camphor*-, m.p. 209·7°; *α-bromocamphor-α*-, m.p. 133·7°; *p*-toluene-, m.p. 181—182°; o-, m- (**II**), and p-*xylene*-, m.p. 207·6—2·08·1°, 145·6—146·0° and 183·7°, respectively; aniline-*p*-, m.p. 184·5—185°; m-*dimethylaminobenzene*-, m.p. 182·4°; *phenol*-p-, m.p. 168·7°; p-*chlorobenzene*-, m.p. 174·9—175·4°; m-*benzenedi*-, m.p. 214·3°; *diphenyl*-4 : 4′-*di*-, m.p. 171·0°; *anthraquinone*-2-, m.p. 211·1°; *naphthalene*-1-, -2-, and -2 : 7-*di*- (**III**), m.p. 136·8°, 190·5—190·8°, and 205° (decomp.), respectively; 1-*naphthylamine*-4, -5-, and -8-, m.p. 195·1° (decomp.), 179·4°, and 300° (decomp.), respectively; 1-*anilinonaphthalene*-8-, m.p. 182—189° (decomp.); 1-*amino*-8-*naphthol*-3 : 6-*di*-, m.p. 312° (decomp.); 2-*naphthylamine*-6- (**IV**), -4′ : 8-*di*-, and -6 : 8-*di*-, m.p. 330° (decomp.), 209—211° (decomp.), and 276° (decomp.), respectively; 1-*naphthol*-2-, -4- (**V**), and -4 : 8-*di*- (**VI**), m.p. 169·4°, 103·4°, and 205·2°, respectively; 2-*naphthol*-6- and -3 : 6-*di*-, m.p. 206·7° and 233·2°, respectively; *benzothiazole*-2-, m.p. 170·5—171°. Satisfactory solid derivatives could not be obtained from *o*-aminophenol-*p*-, phenylhydrazine-*p*-, 2-amino-8-naphthol-6-, 2-naphthylamine-5 : 7-di-, 1-naphthylamine-3 : 6 : 8-tri-, 2-naphthol-8-, 1-naphthol-3 : 8-di-, 2-naphthol-6 : 8-di-, and 1 : 8-dihydroxynaphthalene-3 : 6-di-sulphonic acid. Analytical results for (**II**)—(**VI**) suggest the presence of H_2O of crystallisation but this could not be confirmed by dehydration experiments. The method is satisfactory for mono- and di-sulphonic acids if other functional groups are absent. The presence of phenolic OH or NH_2 reduces but does not preclude the possibility of securing a satisfactory solid derivative. NH_2 is particularly disadvantageous in the naphthalenesulphonic acids. Satisfactory thiuronium derivatives can often be prepared from relatively impure sulphonic acids. It is possible that thiuronium salts can be used in the separation of sulphonic acids, M.p. are corr. H. W.

Quantitative drop analysis. XIII. Formol titration of amino-nitrogen. R. C. Sisco, B. Cunningham, and P. L. Kirk (*J. Biol. Chem.*, 1941, **139**, 1—10).—The sample (~0·05 ml.) of 0·01M-NH_2-acid solution is measured into a porcelain dish. A known amount (~0·01 ml.) of diluted phenolphthalein solution is added, and the solution is titrated with 0·02N-NaOH to a faint pink colour. A vol. of 12—13% aq. CH_2O equal to that of the NH_2-acid solution is added, and the solution is again titrated to a faint pink. A blank determination is also made with distilled H_2O. Separate NH_3 determinations and controlled titrations with known amounts of NH_3 present are used to correct for the presence of NH_3 or NH_4 salts in the sample. The titrations may be carried out electrometrically in the depressed cup of a glass electrode. The sample is adjusted to p_H 7, an equal vol. of CH_2O (adjusted to p_H 5) is added, and the mixture is titrated to p_H 8. The methods are comparable in accuracy with the macro-method. J. W. S.

Chemical determination of vitamin-*C*.—See A., 1941, III, 599.

Effects of salts on activity of *Proteus vulgaris* in removing glucose, and possible sources of error in use as reagent for determination of glucose.—See A., 1941, III, 707.

Determination of carotene.—See A., 1941, III, 594.

Determination of nicotinic acid and vitamin-B_6.—See A., 1941, III, 686.

Cobalt colour reactions of barbiturates.—See A., 1941, III, 697.

Colorimetric determination of citrulline.—See A., 1941, III, 716.

Microchemical detection of nicotine vapour in air. A. I. Burschtein and I. M. Korenman (*J. Appl. Chem. Russ.*, 1940, **13**, 1525—1528).—1—2 l. of air are aspirated through 0·25 ml. of 0·1% H_2SO_4, and a few crystals of $(NH_4)_2SO_4$ and of $KBiI_4$ are added to a drop of the solution on a slide. Characteristic orange micro-crystals of nicotine salt appear when the solution contains $\lessdot$2 p.p.m. of nicotine. R. T.

Determination of guanine and xanthine. G. H. Hitchings (*J. Biol. Chem.*, 1941, **139**, 843—854).—Guanine and xanthine are determined together by the modified phenol reagent of Folin *et al.* (A., 1927, 892). Tissues are extracted by CCl_3·CO_2H, followed by $CuSO_4$–$NaHSO_3$ pptn. Hydroxy-adenine can be similarly determined, but pure adenine and hypoxanthine give no colour with the reagent. Analyses of some tissues are given. A. Li.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

OCTOBER, 1941.

I.—ALIPHATIC.

Nature of the ethylenic linking in olefines containing the carbonyl group. V. V. Razumovski (*J. Gen. Chem. Russ.*, 1940, **10**, 1551—1552).—Theoretical. There is no essential difference between the nature of the >C:C< grouping of compounds >C:C·CO· and of other ethylenic compounds. R. T.

Synthesis of ethylenic, diethylenic, and other hydrocarbons, and their electro-polymerisation. I, II. K. I. Karasev (*J. Gen. Chem. Russ.*, 1940, **10**, 1699—1703, 1704—1712).—I. The alcohols CH_2:$CH·CH_2·CHR·OH$ have been synthesised by Grignard reactions from CH_2:$CH·CH_2·MgCl$ and RCHO (R = Pr$^{\alpha}$, *n*-hexyl, and n-*decyl*, b.p. 140—141°/9 mm.). These alcohols were dehydrated by Tschugaev's method to $\Delta^{\alpha\delta}$-*heptadicne* (**I**), b.p. 100—101·5°, $\Delta^{\alpha\delta}$-*decadiene* (**II**), b.p. 170—171·5°, and $\Delta^{\alpha\delta}$-*tetradecadiene* (**III**), b.p. 110—111°/9 mm.

II. Δ^{α}-Dodecylene (**IV**), (**I**), (**II**), (**III**), *n*-$C_{14}H_{30}$, *ψ*-cymene (**V**), 1 : 1 (**II**)–(**IV**), 3 : 7 (**III**)–(**IV**), and 1 : 1 : 1 (**II**)–(**IV**)–(**V**) were exposed to a silent electric discharge, and the properties of the products were determined periodically. The mol. wt. rose increasingly rapidly in all cases, the I and H vals. fell steadily, except in the case of *n*-$C_{14}H_{30}$, and the content of hydrocarbons with conjugated ethylenic linkings rose to a max., and then fell, owing to cyclisation. R. T.

Catalytic isomerisation of Δ^{α}-butene.—See A., 1941, I, 382.

Conjugated systems. XII. Reaction of α-bromobutadiene with alkyl hypoiodites. Synthesis of α-bromo-γ-alkoxy-derivatives of divinyl and of γ-alkoxyvinylacetylenes. A. A. Petrov (*J. Gen. Chem. Russ.*, 1940, **10**, 1682—1688).—$CHBr$:$CH·CH$:CH_2 and I in ROH in presence of HgO yield ethers $CHBr$:$CH·CH(OR)·CH_2I$ (R = *Me*, b.p. 89—90°/5 mm., *Et*, b.p. 96—96·5°/5 mm., *Pr*$^{\alpha}$, b.p. 103·5—104°/5 mm.), converted by KOH–ROH into the ethers, $CHBr$:$CH·C(OR)$:CH_2 (R = *Me*, b.p. 57—58°/24 mm., *Et*, b.p. 69—71°/24 mm.), together with ethers CH:$C·C(OR)$:CH_2 (R = *Me*, b.p. 87—87·5°, *Et*, b.p. 103·5—104°, *Pr*$^{\alpha}$, b.p. 124—125°), hydrolysis of which with 5% H_2SO_4 gives *Me acetylenyl ketone*, b.p. 83·5—84·5°. R. T.

Kinetics of polymerisation of isoprene on sodium surfaces.—See A., 1941, I, 382.

Reaction of iodine and iron with (I) methyl alcohol, (II) ethyl acetate and benzoate. M. T. Dangjan (*J. Gen. Chem. Russ.*, 1940, **10**, 1668—1669, 1670—1672).—I. Mel and a basic Fe salt are produced when MeOH is added to a mixture of I and Fe.

II. The products obtained similarly from EtOAc or EtOBz (1 hr. at the b.p.) are EtI and $Fe(OAc)_3$ or $Fe(OBz)_3$. R. T.

Synthesis and octane number of certain unsaturated alcohols and diethylenic hydrocarbons. K. I. Karasev and A. V. Chabarova (*J. Gen. Chem. Russ.*, 1940, **10**, 1641—1646).—ε-Methyl-Δ^{α}-hexen-δ-ol (83·4), Δ^{β}-hepten-δ-ol (83·5), Δ^{β}-octen-δ-ol, and ζ-methyl-Δ^{β}-hepten-δ-ol have been prepared by Grignard reactions, and ε-*methyl*-$\Delta^{\alpha\delta}$-*hexadiene* (130·5), b.p. 91—92·5°, $\Delta^{\beta\delta}$-octadiene (102·5), $\Delta^{\beta\delta}$-heptadiene (127·2), and ζ-methyl-$\Delta^{\beta\delta}$-heptadiene (120) were prepared therefrom by dehydration. The figures in parentheses refer to octane nos. R. T.

Derivatives of allylic chlorides. β-Methylglycerol and its derivatives. G. Hearne and H. W. de Jong (*Ind. Eng. Chem.*, 1941, **33**, 940—943; cf. A., 1941, II, 158).—$(CH_2Cl)_2CMe·OH$ (**I**) and $(CH_2Cl)_3C·OH$ with CaO–H_2O at 60° yield respectively β-methyl-, b.p. 122° [which with NH_3 yields αγ-diamino-β-methylpropanol, b.p. 81·5—83·5°/4 mm., also prepared from (**I**), NH_3, and NaOH], and *β-chloromethyl-epichlorohydrin*, b.p. 89·5°/31 mm., hydrated (hot very dil. H_2SO_4) to β-methyl-, b.p. 80°/1·6 mm. (which with NH_3 yields γ-amino-β-methylpropane-αβ-diol, m.p. ~35°), and *β-chloromethyl-glycerol monochlorohydrin*, b.p. 120°/1·1 mm., which with 15% NaOH at room temp. yield β-methyl-, b.p. 68°/25 mm., and *β-chloromethyl-glycidol*, b.p. 85°/1 mm., hydrolysed (0·5% H_2SO_4 at 35—40° and 0·1% H_2SO_4 at 100° respectively) to β-methyl-, b.p. 115—120°/1·6 mm. [also obtained from (**I**) with $NaHCO_3$ or from $CH_2Cl·CMe(OH)·CH_2·OH$ with NaOH], and *β-chloromethyl-glycerol* (**II**), b.p. 150°/0·6 mm. Distillation of (**I**) or any of its products with 12% H_2SO_4 yields methylacraldehyde. (**II**) is hydrolysed (dil. NaOH) to $OH·C(CH_2·OH)_3$. A table of products obtainable from $CH_2Cl·CMe$:CH_2 is given. A. Li.

High mol. wt. fatty acid derivatives. II. Sulphides, sulphoxides, and sulphones. B. A. Hunter (*Iowa State Coll. J. Sci.*, 1941, **15**, 215—221).—*n*-$C_{18}H_{37}I$ when boiled (8 hr.) with an excess of Na_2S–EtOH yields n-*octadecyl sulphide* (**I**), m.p. 68—69°, which when treated with CrO_3–hot AcOH or with hot dil. HNO_3 gives n-*octadecyl sulphoxide* (**II**), m.p. 99—100°. (**I**) or (**II**) with H_2O_2 in hot AcOH, or (**I**) with fuming HNO_3 for 1 hr. at 100°, gives n-*octadecyl sulphone*, m.p. 105·5—106·5°. When (**II**) is boiled with Zn dust–AcOH for 20 hr. it gives (**I**); the sulphone, similarly treated, is unchanged. n-*Hexadecyl*, m.p. 57—58°, n-*tetradecyl*, m.p. 49—50°, and n-*dodecyl sulphide*, m.p. 40—40·5°, were prepared like (**I**) and similarly yielded *sulphoxides*, m.p. 97—98°, 95—96°, and 89—90°, respectively, and *sulphones*, m.p. 100—100·5°, 99·5—100°, and 94·5—95·5°, respectively. J. L. D.

Quantitative studies of the oxidation of fatty acids by hydrogen peroxide. Interpretation of the reaction mechanism. R. H. Allen and E. J. Witzemann (*J. Amer. Chem. Soc.*, 1941, **63**, 1922—1927).—The CO_2, AcOH, $COMe_2$, other ketones, and aldehydes formed by oxidation of *n*-C_{2-7} acids by H_2O_2 in boiling aq. Na_2HPO_4, NH_3, and $(NH_4)_2HPO_4$ are determined, conditions being such that complete oxidation occurs. Results are interpreted as substantiating the view that the NH_3 or phosphate accelerates dehydrogenation of the org. substance so that the reaction, $H_2O_2 + 2H \rightarrow 2H_2O$, predominates over $H_2O_2 \rightarrow 2H + O_2$. R. S. C.

Resolution of enantiomorphs. I. Rectification. M. E. Bailey and H. B. Hass (*J. Amer. Chem. Soc.*, 1941, **63**, 1969—1970).—Partial resolution of alcohols and acids is effected by fractional distillation of esters with active acids or alcohols, respectively. Examples are $CHMeEt·CO_2H$ from *dl*-$CHMeEt·CO_2·CH_2·CHMeEt$-*d* or *l*-menthyl *dl*-α-methylbutyrate; $OMe·CHMe·CO_2H$ from its *l*-menthyl ester; CHMeEt·OH from the *l*-lactate, *l*-$OAc·CHMe·CO_2·CHMeEt$-*dl*, or *l*-$EtCO_2·CHMe·CO_2·CHMeEt$-*dl* (gives 86% pure *d*-CHMeEt·OH); $CHMePr^{\alpha}·OH$ from the *l*-lactate; $CHEtBu^{\alpha}OH$ from *d*-$CHMeEt·CO_2·CHEtBu^{\alpha}$-*dl*. R. S. C.

Acyl derivatives of iodine. T. W. H. Oldham and A. R. Ubbelohde (*J.C.S.*, 1941, 368—375).—$C_nH_{2n+1}·CO_2Ag$ (*n* = 2, 3, 5, 7, 11, 15, and 17) with I in anhyd. inert solvent yield I triacyls [? with some IO·CO·R and $I(O·CO·R)_5$], m.p. ~120° with production of OR·CO·R, CO_2, I, RI, and (?) traces of hydrocarbon. Thermal decomp. of these in anhyd. C_6H_6 or CCl_4 (PhMe or xylene causes side reactions) yields 80% (on the acid used) of RI. The reaction is explained in terms of

primary liberation of free acyl radicals, and is recommended for the decarboxylation of acids or the prep. of odd-C acyl iodides. The acyls are readily hydrolysed, the reaction with long-chain acyls being: $I(O{\cdot}CO{\cdot}R)_3 + 3H_2O \rightarrow I(OH)_3 + 3RCO_2H$; $5I(OH)_3 \rightarrow 3HIO_3 + 6H_2O$. A. LI.

Hydrogenation of allyl crotonate, fumarate, and oleate, with platinum and palladium catalysts. V. P. Golendeev (*J. Gen. Chem. Russ.*, 1940, **10**, 1539—1542).—Hydrogenation of the allene radical precedes that of the acid radical. R. T.

Methylneopentylacetic (αγγ-trimethyl-*n*-valeric) acid, its methyl ester, amide, and anilide. F. C. Whitmore, C. I. Noll, J. W. Heyd, and J. D. Surmatis (*J. Amer. Chem. Soc.*, 1941, **63**, 2028).—Di*iso*butylene and $Na_2Cr_2O_7$–H_2SO_4 give 6% of *αγγ-trimethyl*-n-*valeric acid* (**I**), b.p. 217·4°/730 mm. (*Me* ester, b.p. 162·25°/730 mm.), which by way of the acid chloride ($SOCl_2$) gives the *amide*, m.p. 123°, and *anilide*, m.p. 117·5°. $CH_2Bu^{\gamma}{\cdot}CH{:}CH_2$ (prep. from $MgBu^{\gamma}Cl$ and $CH_2{:}CH{\cdot}CH_2Br$ in Et_2O) with HBr and $NHPh_2$ gives $CH_2Bu^{\gamma}{\cdot}CHMeBr$ (66%), b.p. 56—60°/29—39 mm., the Grignard reagent from which gives (**I**). $CH_2Bu^{\gamma}{\cdot}CHMe{\cdot}OH$ and anhyd. HCl give (22 weeks) $CH_2Bu^{\gamma}{\cdot}CHMeCl$, b.p. 63—65°/85 mm., and thence (Grignard) (**I**). R. S. C.

Rearrangement [migration] of allyl groups in three-carbon systems. I. A. C. Cope, (Misses) K. E. Hoyle, and D. Heyl. **II.** A. C. Cope,•(Misses) C. M. Hofmann, and E. M. Hardy (*J. Amer. Chem. Soc.*, 1941, **63**, 1843—1852, 1852—1857).—I. Heating causes rearrangement of $CRR'{:}CR''{\cdot}CX(CN)_2$, $CRR'{:}CR''{\cdot}CX(CN){\cdot}CO_2Et$ (*A*), and $CRR'{:}CR''{\cdot}CX(CO_2Et)_2$ to $CRR'X{\cdot}CR''{:}C(CN)_2$, $CRR'X{\cdot}CR''{:}C(CN){\cdot}CO_2Et$, and $CRR'X{\cdot}CR''{:}C(CO_2Et)_2$, respectively (X = allyl) (cf. A., 1940, II, 152). The reactions are of first order, indicating their intramol. nature. The order of decreasing rates is that given above, which is also that of electron attraction at $C_{(\alpha)}$. Branching of R or R' decreases the rate of change sterically. Methods of prep. of the starting materials are generally slight modifications of those previously detailed (A., 1939, II, 48; *loc. cit.*). Structures are confirmed by *n*. *Et α-cyano-α-*Δ^1-cyclo*hexenyl-*Δ^{γ}-*pentenoate*, b.p. 110—111°/1 mm., at 230° or 170° gives *Et* 2-*allyl*cyclo*hexylidenecyanoacetate* (**I**), b.p. 170—171°/13 mm., hydrolysed by conc. aq. NH_3 at room temp. to 2-allyl*cyclo*hexanone (**II**), b.p. 78—79°/11 mm. (oxime, m.p. 70—70·5°). Et *cyclo*hexanone-2-carboxylate (prep. modified), $CH_2{:}CH{\cdot}CH_2Br$ (**III**), and NaOEt–EtOH give *Et* 2-*allyl*cyclo*hexanone-2-carboxylate*, b.p. 127—128°/11 mm., hydrolysed with difficulty (KOH) to (**II**). Heating (**II**), $CN{\cdot}CH_2{\cdot}CO_2Et$, NH_4OAc, and AcOH in C_6H_6 with removal of H_2O gives 71% of (**I**). *Et α-cyano-β-methyl-α-allyl-*Δ^{β}-n-*hexenoate*, b.p. 91—92°/1 mm., at 170° gives *Et α-cyano-β-methyl-γ-ethyl-*$\Delta^{\alpha\epsilon}$-*heptadienoate*, b.p. 160—161°/21 mm., hydrolysed by aq. NH_3 to *γ-ethyl-*Δ^{ϵ}-n-*hexen-β-one*, b.p. 155—156° (2 : 4-*dinitrophenylhydrazone*, m.p. 51·5—53°), also obtained from $CH_2{:}CH{\cdot}CH_2{\cdot}CHAc{\cdot}CO_2Et$ (**IV**) by way of *Et α-acetyl-α-ethyl-*Δ^{γ}-*pentenoate*, b.p. 118—119°/23 mm. *Et α-cyano-β-methyl-α-allyl-*Δ^{β}-n-*octenoate*, b.p. 106—107°/1 mm., at 200° gives *Et α-cyano-β-methyl-γ-allyl-*Δ^{α}-n-*octenoate*, b.p. 173—174°/18 mm., hydrolysed by aq. NH_3 to *γ-allyl*-n-*heptan-β-one*, b.p. 190—191°/760 mm., 90—91·5°/21 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 47·5—49°), also obtained from (**IV**) by way of *Et α-acetyl-α-allyl*-n-*hexoate*, b.p. 138—139°/22 mm. *Et α-cyano-*$\beta\delta$*-dimethyl-α-allyl-*Δ^{β}-*hexenoate*, b.p. 100—101°/1·5 mm., at 170° gives *Et α-cyano-β-methyl-γ-*iso*propyl-*$\Delta^{\alpha\epsilon}$-*heptadienoate*, b.p. 165—167°/24 mm., hydrolysed to *γ-*iso*propyl-*Δ^{ϵ}-n-*hexen-β-one*, b.p. 168—169°/760 mm., 67—68°/18 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 77—78·5°), also obtained from (**IV**) by way of *Et α-acetyl-α-*iso*propyl-*Δ^{γ}-n-*pentenoate*, b.p. 118—120°/17 mm. *Et α-cyano-α-α'-phenylvinyl-*Δ^{γ}-*pentenoate*, b.p. 101°/$\sim 10^{-5}$ mm., at 170° gives very rapidly *Et α-cyano-β-phenyl-*$\Delta^{\alpha\epsilon}$-*heptadienoate*, b.p. 138—139°/0·5 mm., hydrolysed to $COPh{\cdot}[CH_2]_2{\cdot}CH{:}CH_2$, b.p. 136—137°/24 mm. (semicarbazone, new m.p. 157—157·5°). *Et α-cyano-β-ethyl-α-allyl-*Δ^{β}-*pentenoate*, b.p. 90—91°/1 mm., at 200° gives *Et α-cyano-γ-methyl-β-ethyl-*$\Delta^{\alpha\epsilon}$-*heptadienoate*, b.p. 162—163°/25 mm., hydrolysed to *δ-methyl-*Δ^{ζ}-*hepten-γ-one* (**V**), b.p. 153·5—154° (2 : 4-*dinitrophenylhydrazone*, m.p. 79·5—81°), also obtained from $COEt_2$ by (**III**) and $NaNH_2$ in Et_2O. Δ^1-cyclo*Hexenylallylmalononitrile* [prep. as for (*A*); purification by 20% $NaHSO_3$], b.p. 58—60°/$\sim 10^{-5}$ mm., at 175° gives very readily 2-*allyl*cyclo*hexylidenemalononitrile*, b.p. 109—110°/0·5 mm., hydrolysed to (**IV**). *Allyl-α-ethyl-propenylmalononitrile*, b.p. 40—42°/$\sim 10^{-5}$ mm., at 150° gives *β-methyl-α-ethyl-*Δ^{δ}-n-*pentenylidenemalononitrile*, b.p. 148—149°/25 mm., hydrolysed to (**V**). *Et*$_2$ *allylpropenylmalonate*, b.p. 79—80°/1 mm., at 200° gives *Et*$_2$ *β-methyl-*Δ^{δ}-n-*pentenylidenemalonate*, b.p. 144—145°/18 mm., hydrogenated (Pd–C) to *Et*$_2$ *β-methyl*-n-*amylmalonate* (**VI**), b.p. 146—147°/24 mm. When $CHMePr^{\alpha}{\cdot}CHO$ (prep. with difficulty from $CHEt{:}CMe{\cdot}CHO$ by H_2–Pd–C in EtOH), $CH_2(CO_2Et)_2$, piperidine, and AcOH are heated in boiling C_6H_6 with removal of H_2O, *Et*$_2$ *β-methyl*-n-*pentylidenemalonate*, b.p. 147—149°/23 mm., is obtained; this is hydrogenated (Pd–C; EtOH) to (**VI**), which is identified by conversion by $CO(NH_2)_2$ and NaOEt into 5-*β-methyl*-n-*amylbarbituric acid*, m.p. 201—201·5°. $CHEt{:}CH{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}CH{:}CH_2$ at 200° gives *Et*$_2$ *β-ethyl-*Δ^{δ}-*pentenylidenemalonate*, b.p. 143—144°/13 mm., hydrogenated to *Et*$_2$ *β-ethyl*-n-*amylmalonate* (**VII**), b.p. 94—95°/0·5 mm., which is characterised as 5-*β-ethyl*-n-*amylbarbituric acid*, m.p. 176·5—177°. (**VII**) is also obtained from $CHEt{:}CH(CO_2Et)_2$ by way of $CHPr^{\alpha}(CO_2Et)_2$, $CEtPr^{\alpha}(CO_2Et)_2$ (by H_2–Cu–Ba chromite; 250°), $CHEtPr^{\alpha}{\cdot}OH$, and $CHEtPr^{\alpha}Br$. *Et*$_2$ *allyl-γ-methyl-*Δ^{α}-*butenylmalonate*, b.p. 111—112°/2 mm., and Δ^1-cyclo*hexenylallylmalonate*, b.p. 109°/0·5 mm., rearranged at 200° to mixtures, but hydrolysis of the products from the latter gives (**V**) by the usual reaction.

II. Occurrence of inversion ($CHR{:}CH{\cdot}CH_2{\cdot} \rightarrow CHR{\cdot}CH{:}CH_2{\cdot}$) during the isomerisations described above is proved. The intramol. nature of the reaction is confirmed by absence of interchange of groups during rearrangement of mixtures. *Et*$_2$ iso*propenyl-*Δ^{γ}-*butenylmalonate* (**VIII**), b.p. 98—100°/2 mm., is obtained by heating $CMe_2{:}C(CO_2Et)_2$, $CHMe{:}CH{\cdot}CH_2Br$ (**IX**), and $NaNH_2$ in PhMe and shaking the product with conc. aq. NH_3 at room temp. Its structure is proved by hydrogenation and subsequent conversion into 5-*iso*propyl-5-*n*-butylbarbituric acid. At 185°/vac. it gives *Et*$_2$ *αγ-dimethyl-*Δ^{δ}-*pentenylidenemalonate*, b.p. 161—163°/27 mm., the structure of which is proved by hydrolysis (aq. NH_3) to *δ-methyl-*Δ^{ϵ}-*hexen-β-one*, b.p. 137—138° (*semicarbazone*, m.p. 112·5—113·5°), and hydrogenation thereof to $COMe{\cdot}CH_2{\cdot}CHMeEt$ (also obtained from $CHPr^{\beta}Ac{\cdot}CO_2Et$ by way of *Et* iso*propyl*-sec.-*butylacetoacetate*, b.p. 98—99°/11 mm.). $CHMe{:}CMe{\cdot}CH(CN){\cdot}CO_2Et$, (**IX**), and NaOEt–EtOH give *Et α-cyano-α-α'-methylpropenyl-*Δ^{γ}-*hexenoate* (**X**), b.p. 109—111°/3 mm. (structure proved by hydrogenation and then conversion into 5-*n*-butyl-5-α-methylpropenyl- and 5-*n*-butyl-5-*sec.*-butyl-barbituric acid), which at 180°/vac. gives *Et α-cyano-*$\beta\gamma\delta$*-trimethyl-*$\Delta^{\alpha\epsilon}$-*heptadienoate*, b.p. 157—160°/23 mm.; the structure of the product is proved by hydrolysis to *γδ-dimethyl-*Δ^{ϵ}-n-*hexen-β-one*, b.p. 151—154° (*semicarbazone*, m.p. 89—90°), hydrogenated (1·009 H_2) to $COMe{\cdot}[CHMe]_2{\cdot}CH{:}CH_2$ [semicarbazone, m.p. 136·5—137·5° (lit. 119°, 124—126°), also obtained from $CHMeEt{\cdot}CMeAc{\cdot}CO_2Et$]. Heating $CHBu^{\alpha}{:}CMe{\cdot}C(CH_2{\cdot}CH{:}CH_2)(CN){\cdot}CO_2Et$ with (**VIII**) or (**X**) at 193·1 ± 0·5° (both pairs rearrange at equal rates at this temp.) gives only the products from each reactant alone, as is proved by fractionation, hydrolysis of fractions, and identification of the ketones. Similar proof by use of cyanoacetates and malonates was impracticable as the products from the former do not react with $NaHSO_3$ and are thus inseparable. $CH_2{:}CH{\cdot}CH_2{\cdot}C(CO_2Et)_2{\cdot}CMe{:}CH_2$ at 180—190° gives *Et*$_2$ *α-methyl-*Δ^{γ}-*pentenylidenemalonate*, b.p. 134—136°, hydrolysed to $CH_2{:}CH{\cdot}[CH_2]_2{\cdot}COMe$. Attempts to prepare various other alkylated cyanoacetates and malonates failed. R. S. C.

Oxidation of pyruvic acid in presence of glycine.—See A., 1941, III, 601.

Condensation of dicarboxylic esters with oxalic ester in presence of sodium. III. Sebacic ester. IV. Nonanedicarboxylic ester. M. A. Zakutskaja. **V. Decanedicarboxylic ester.** M. A. Zakutskaja and F. C. Solomachina (*J. Gen. Chem. Russ.*, 1940, **10**, 1553—1558, 1559—1561, 1562—1564). —III. Et_2 sebacate (**I**), $Et_2C_2O_4$ (**II**), and NaOEt in Et_2O (10 hr. at 100°) yield *Et*$_3$ *octane-*$\alpha\alpha\theta$*-tricarboxylate* (**III**), b.p. 190—195°/7·5 mm., which with EtI affords *Et*$_3$ *decane-*$\gamma\gamma\kappa$*-tricarboxylate*, b.p. 185—190°/10 mm. When (**I**), (**II**), and Na in EtOH are shaken for 2 hr., Et_2O is added, and the mixture is heated at the b.p. for 10 hr., *Et*$_3$ *α-oxalosebacate* (**IV**) is formed; it decomposes at the b.p. to yield (**III**). (**IV**) is converted into *α-ketononane-*$\alpha\iota$*-dicarboxylic acid*, m.p. 95—98° (*semicarbazone*, m.p. 128—130°; *phenylhydrazone*, m.p. 110—112°), by 30% HCl at the b.p.

IV. Et_2 nonane-$\alpha\iota$-dicarboxylate and (**II**) are condensed, as above, to *Et_3 α-ketodecane-αβκ-tricarboxylate*, decomp. at the b.p. to *Et_3 nonane-ααι-tricarboxylate*, b.p. 178—183°/6 mm., which with 10% KOH (15 hr. at 100°) affords nonane-$\alpha\iota$-dicarboxylic acid.

V. Et_2 decane-$\alpha\kappa$-dicarboxylate, condensed as above, yields *Et_3 α-ketoundecane-αβλ-tricarboxylate*, decomp. at the b.p. to *Et_3 decane-ααλ-tricarboxylate*, b.p. 185—190°/5 mm., converted by 10% KOH at 100° into decane-$\alpha\kappa$-dicarboxylic acid. R. T.

Influence of ascorbic acid on oxidation of tyrosine by ultra-violet light.—See A., 1941, III, 598.

α-Guanidino-γ-methylthiolbutyric acid (guanidinomethione). F. Irreverre and M. X. Sullivan (*J. Amer. Chem. Soc.*, 1941, **63**, 2027).—This *compound*, m.p. 193—194°, is obtained from *dl*-methionine and SMe·C(:NH)·NH_2,HI in NaOH at room temp. R. S. C.

Preparation of formaldehyde from methane. A. P. Kreshkov (*J. Gen. Chem. Russ.*, 1940, **10**, 1605—1611).—Cl_2–CH_4 mixtures when passed over CuCl–C catalyst at 700° give CH_2O in 10% yield. At other temp. or with other catalysts ($BaCl_2$–C, CuCl–, V_2O_5–, or $CuCl_2$–pumice) the yields are much smaller. The low yields are ascribed to further oxidation of CH_2O, and to parasitic reactions of Cl_2. R. T.

Condensation of methoxyacetaldehyde to 2 : 4-dimethyl-aldotetrose. Methoxy- and ethoxy-acetaldehyde. C. D. Hurd and J. L. Abernethy (*J. Amer. Chem. Soc.*, 1941, **63**, 1966—1968).—Distillation (reflux condenser at 75—80°) of OMe·$[CH_2]_2$·OH and aq. $K_2Cr_2O_7$–H_2SO_4 in CO_2 gives 16·7% of OMe·CH_2·CHO (**I**), isolated as azeotrope with 12·8% of H_2O. OEt·$[CH_2]_2$·OH gives similarly 10% of OEt·CH_2·CHO (**II**) as azeotrope with 21·8% of H_2O. The apparent mol. wt. of (**I**) and (**II**) in freezing C_6H_6 increases with time owing to polymerisation (not inhibited by quinol). In aq. K_2CO_3 (or, less well, KCN) at 0°, (**I**) gives 2 : 4-*dimethylaldotetrose*, b.p. 77—80°. OH·CHMe·CH_2·CH(OMe)$_2$, Na wire, and MeI in Et_2O give *β-methoxy-n-butaldehyde Me_2 acetal*, b.p. 90—96°/17 mm. R. S. C.

Synthesis of asymmetrical allenic compounds of the aliphatic series by the acetylene–allene rearrangement. A. E. Favorski and P. A. Tichomolov (*J. Gen. Chem. Russ.*, 1940, **10**, 1501—1506).—CBu$^{\gamma}$:C·MgBr and CH_2AcCl in Et_2O yield *εε-dimethyl-β-chloromethyl-Δγ-hexin-β-ol*, converted by KOH in Et_2O into *αβ-oxido-βεε-trimethyl-Δγ-hexine*, b.p. 156°. This, when heated at the b.p. with $ZnCl_2$, yields *εε-dimethyl-$\Delta^{\beta\gamma}$-hexadien-β-al*, b.p. 57·8—58·8°/20 mm. [*semicarbazone*, m.p. 156—157° (decomp.)]. R. T.

Potentiometric study of differentiating action of ketones. A. M. Schkodin (*J. Gen. Chem. Russ.*, 1940, **10**, 1694—1698).—0·1—1% of H_2SO_4 in 75% OH·CHMe·CO_2H can be determined in $COMe_2$ or COMeEt by electro-titration with 0·2N-NaOH in EtOH. $(OH·CHMe·CO_2)_2Ca$ in 50% $COMe_2$ can be determined by titration with 0·01N-H_2SO_4 in 75—90% $COMe_2$. R. T.

Oxidation of organic compounds by selenium dioxide. VIII. Oxidation of isomeric ketones. N. N. Melnikov and M. S. Rokitzkaja (*J. Gen. Chem. Russ.*, 1940, **10**, 1713—1716).—The velocity coeffs. of the reaction of oxidation of Me amyl and hexyl ketones by SeO_2 in 75% AcOH at 20° are: COMe·CH_2Bu$^{\beta}$ 0·91, COMe·CH_2·CHMeEt 0·99, COMe·C_5H_{11}-*n* 1·27 × 10^{-7}, COMe·$[CH_2]_2$·CHMeEt 1·05, COMe·C_6H_{13}-*n* 1·2, COMe·$[CH_2]_2$·Bu$^{\beta}$ 1·4, and COMe·CH_2·CHMePr$^{\alpha}$ 1·5 × 10^{-7}. It is concluded that enolisation is more pronounced in the case of ketones having an odd no. of CH_2 groups between the CO and the *sec.* C than when this no. is even, or when there is no *sec.* C. R. T.

Photolysis of keten and structure of methylene.—See A., 1941, I, 382.

Action of magnesium *iso*amyl bromide on mesityl oxide. II. V. I. Esafov and M. V. Smirnov (*J. Gen. Chem. Russ.*, 1940, **10**, 1535—1538).—COMe·CH:CMe_2 and *iso*-C_5H_{11}·MgBr in Et_2O at −15° and −60° yield *βδη-trimethyl-$\Delta^{\beta\delta}$-octadiene*, b.p. 165—168°, which condenses with maleic anhydride to 4 : 6 : 6-*trimethyl*-3-iso*amyl*-1 : 2 : 3 : 6-*tetrahydrophthalic acid*, m.p. 177°. R. T.

Formation of polyhydroxydialdehydes. II. *d*-Lyxotrihydroxyglutaric dialdehyde and its derivatives. K. Iwadare (*Bull. Chem. Soc. Japan*, 1941, **16**, 144—149; cf. A., 1941, II, 160).—Partial hydrolysis (H phthalate buffer, p_H 4·4, at 140—150°) of 2 : 3 : 5 : 6-di*iso*propylidene- yields 2 : 3-*iso*propylidene-*d*-mannofuranose (Freudenberg *et al.*, A., 1928, 1222), m.p. 80·5—82° (corr.), $[\alpha]_D^{15}$ +4·5° in H_2O (5 min.), −3·7° (40 hr.) (triacetate, m.p. 58·5—59°). Oxidation of this [$Pb(OAc)_4$ in AcOH at 60—65°] yields CH_2O (70% of theoretical), or [$Pb(OAc)_4$ in C_6H_6 at 70°] *d*-lyxotrihydroxyglutardialdehyde, $[\alpha]_D^{15}$ ~+5° in H_2O [*bisphenylhydrazone*, m.p. 168·5—169° (corr.; decomp.)], oxidised (Br) to the glutaric acid (*Sr* salt). A. Li.

General carbohydrate reaction. L. Rosenthaler (*Pharm. Acta Helv.*, 1940, **15**, 265).—The pink colour produced on NH_2Ph–AcOH paper, which is sp. for the reaction between pentoses, pentosecarboxylic and ascorbic acids with HCl, is also given by the following when 70—80% H_2SO_4 is substituted for HCl; glucose (**I**), fructose, galactose, maltose, sucrose, lactose, glycogen, lichenin, inulin, starch, cellulose, and some glucosides. Mannitol and sorbitol give no reaction. 1 μg. of (**I**) can be detected. E. H. S.

Glycosidic components of the flowers of *Butea frondosa*. P. B. R. Murti and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **13, A**, 395—398).—The isolation is described of butrin, m.p. 194—195° (decomp.), hydrolysed by boiling 7% H_2SO_4 to butin with a small proportion of butein. Very small amounts have been obtained of a phytosterolin, $C_{34}H_{62}O_6$, m.p. 260—262° (decomp.), hydrolysed to sitosterol and glucose (**I**). A *heteroside*, $C_{23}H_{40}O_{10}$, m.p. 236—237° (decomp.), apparently related to the resinols, has been isolated; it is hydrolysed to (**I**) and a colourless *aglucon*, m.p. 220°. H. W.

Compounds of salts of bivalent manganese with pyridine and ethylenediamiue.—See A., 1941, I, 385.

Azeotropic mixture of α-diethylaminobutan-γ-ol and acetic acid. K. Tsuda, A. Oguri, and S. Fukushima (*J. Pharm. Soc., Japan*, 1941, **61**, 36—38).—The mixture has b.p. 83·5°/7 mm., and contains AcOH 43·6% and NEt_2·$[CH_2]_2$·CHMe·OH 56·4% (mol. ratio, 0·65 : 0·35). H. W.

Hydrogenation of α-diethylaminobutan-γ-one. K. Tsuda, S. Fukushima, and A. Oguri (*J. Pharm. Soc., Japan*, 1941, **61**, 31—36).—$COMe_2$, NH_2Et_2Cl, 33% CH_2O, and H_2O at 100° (25—30 hr. preferably at p_H 1·2) give a 50—55% yield of *α-diethylaminobutan-γ-one* (**I**), b.p. 76·5°/14 mm. [hygroscopic *hydrochloride* (**II**), m.p. 74—77°; *platinichloride*, decomp. 180°; non-cryst. aurichloride], and a very unstable by-product, b.p. 84—90°/7 mm., from which a platinichloride or aurichloride could not be derived because of its reducing properties. (**I**) is reduced by Na–Hg in boiling moist Et_2O to *α-diethylaminobutan-γ-ol* (**III**), b.p. 68·5°/7 mm. (*hydrochloride*, m.p. 118—120°; *platinichloride*, decomp. 184°; non-cryst. aurichloride), converted by $SOCl_2$ at 50° into γ-chloro-α-diethylaminobutane (*hydrochloride*, m.p. 82°; *platinichloride*, decomp. 182°; *aurichloride*, m.p. 94—96°). Absorption of 1 mol. of H_2 by (**I**) in MeOH containing Pd–C gives a 65% yield of $NHEt_2$ but no (**III**) whereas no absorption is observed with (**II**) in MeOH or AcOH. In presence of PtO_2 in MeOH (**I**) absorbs H_2 with formation of 51% of (**III**) and 45% of NH_2Et_2Cl. In AcOH with PtO_2 the yield of (**III**) is increased to 70—80% and that of NH_2Et_2Cl is diminished to 10%; this is also true of reduction in dil. AcOH, which occurs very slowly. HCl, as acid, inhibits hydrogenation. The best method consists in the use of PtO_2 in AcOH. α-Diethylaminopentan-δ-one does not absorb H_2 in MeOH containing Pd–C. With PtO_2 in MeOH or AcOH it affords 70—80% of *α-diethylaminopentan-δ-ol*, b.p. 85—87°/5 mm. (hygroscopic *hydrochloride*, m.p. 86—88°; non-cryst. aurichloride; *platinichloride*, m.p. 126—129°), but no $NHEt_2$. H. W.

Kinetics of alcoholysis of polyglycine esters.—See A., 1941, I, 381.

Racemisation of glutamic acid with alkalis. L. E. Arnow and J. C. Opsahl (*Science*, 1941, **93**, 214—215).—*l*(+)-Glutamic acid (**I**) is slowly racemised by boiling in 4N- and 8N-NaOH. When heated in an autoclave at 120°, a $Ba(OH)_2$ solution of (**I**) becomes optically inactive in ~88 hr. L. S. T.

Action of diazobenzene on alkylacetoacetic esters as a method of preparation of phenylhydrazones of α-keto- and α-amino-acids. V. Synthesis of valine. V. V. Feofilaktov and

V. N. Zaitzeva (*J. Gen. Chem. Russ.*, 1940, **10**, 1391—1392). —CHPr$^{\beta}$Ac·CO_2Et and PhN_2Cl yield a product, not isolated, which is hydrolysed to NHPh·N:CPr$^{\beta}$·CO_2H, reduced by Zn in aq.-alcoholic HCl to *dl*-valine. R. T.

Methionine. VI. *dl*-Methionine sulphone. G. Toennies and J. J. Kolb (*J. Biol. Chem.*, 1941, **140**, 131—134).—*dl*-Methionine with H_2O_2 in presence of MoO_4'' and acid ($HClO_4$) gives 90% of the *sulphone* (Cu salt; picrate), the reaction rate being $\propto [MoO_4'']$. A. Li.

Absorption of oxygen by glutathione in alkaline solutions. M. B. Young, H. A. Young, and M. Kleiber (*J. Amer. Chem. Soc.*, 1941, **63**, 1488).—At p_H 9 and with [H·] 0·171, glutathione absorbs approx. sufficient O_2 to give the disulphide and sulphinic acid, respectively. Increasing the $[CuSO_4]$ and O_2 pressure increases the reaction rate. R. S. C.

High mol. wt. fatty acid derivatives. III. Carboxylic acid salts and amides of *n*-dodecylamine and *n*-octadecylamine. B. A. Hunter (*Iowa State Coll. J. Sci.*, 1941, **15**, 223—230).—Equimol. amounts of n-$C_{18}H_{37}$·NH_2 and stearic acid in warm light petroleum (in some cases EtOH) gave *N-n*-octadecylammonium stearate, m.p. 89·5—90·5°. The following were prepared similarly: N-n-*octadecylammonium formate*, m.p. 78·5—79·5°, *acetate*, m.p. 84·5—85°, *propionate*, m.p. 78·5—79°, n-*butyrate*, m.p. 71—71·5°, n-*valerate*, m.p. 60—61°, *hexoate*, m.p. 55—56°, *octoate*, m.p. 57·5—58°, *decoate*, m.p. 62—62·5°, *laurate*, m.p. 68—69°, *myristate*, m.p. 78—78·5°, *palmitate*, m.p. 85—85·5°, *benzoate*, m.p. 65—66°, *anthranilate*, m.p. 92·5—93·5°, *α-furoate*, m.p. 91—92°, *cinnamate*, m.p. 80·5—81·5°, *salicylate*, m.p. 73·5—74°, *phenylacetate*, m.p. 85—85·5°, *oxalate*, m.p. 203—205°, *α-naphthoate*, m.p. 109—110°, and *2-dibenzfurancarboxylate*, m.p. 88—89°; N-n-*dodecylammonium acetate*, m.p. 67—68°, *propionate*, m.p. 56—57°, *laurate*, m.p. 72—73°, *myristate*, m.p. 72·5—73°, *palmitate*, m.p. 72—73°, *stearate*, m.p. 69—70°, *α-furoate*, m.p. 72·5—73°, *phenylacetate*, m.p. 68·5—69·5°, *α-naphthoate*, m.p. 114—115°, *chloroacetate*, m.p. 65—66°, *2-dibenzfurancarboxylate*, m.p. 87·5—88·5°, and *cinnamate*, m.p. 53·5—55°. The above salts are converted into amides by heating at 225—250° for 15—30 min. in N_2. The following are new: *form-*, m.p. 68—68·5°, *propion-*, m.p. 77—77·5°, n-*butyr-*, m.p. 76—76·5°, n-*valer-*, m.p. 76—76·5°, *hexo-*, m.p. 78—78·5°, *octo-*, m.p. 79—79·5°, *deco-*, m.p. 83—83·5°, *α-furo-*, m.p. 79·5—80·5°, *cinnam-*, m.p. 90—91°, *salicyl-*, m.p. 74·5—75·5°, *phenylacet-*, 94·5—95°, *ox-*, m.p. 120—121°, *α-naphtho-*, m.p. 89·5—90°, and *2-dibenzfurancarboxyl*-n-*octadecylamide*, m.p. 118—118·5°; *propion-*, m.p. 53—53·5°, *α-furo-*, m.p. 57—58°, *α-naphtho-*, m.p. 71—72°, *2-dibenzfurancarboxyl-*, m.p. 112—113°, and *cinnam*-n-*dodecyl-amide*, m.p. 74—74·5°. J. L. D.

Oxalenediamidoxime (oxamidedioxime). II. R. Chatterjee (*J. Indian Chem. Soc.*, 1941, **18**, 19—24; cf. A., 1939, **I**, 219).—$(NH_2·C:N·OH)_2$ [or RH_2 where H indicates the replaceable H of the N·OH groups] (**I**) (2 mols.) and $NiCl_2$ (1 mol.) in slightly ammoniacal solution yield Ni bisoxamidedioxime (**II**), $Ni(RH)_2$ (+$2H_2O$, lost at 110—120°) (diamagnetic), methylated [MeI (2 mols.) in EtOH, but not Me_2SO_4] to a *methiodide*, $Ni(RH)_2$,2MeI (formula discussed). (**II**) is probably a planar mol. in which the auxiliary linkings through N appear to occupy *trans*-positions. (**I**) (2 mols.) and aq. $NiCl_2$ (1 mol.) in slightly acid (HCl) solution afford the blue *Ni bisoxamidedioxime chloride*, $2RH_2$,$NiCl_2$,$6H_2O$ (paramagnetic), converted by aq. NH_3 into (**II**) (reaction is reversible). The following are prepared: Cu^{II} bisoxamidedioxime, $Cu(RH)_2$; Cu^{II} *oxamidedioxime chloride*, RH_2,$CuCl_2$ [from (**I**) (1 mol.) and $CuCl_2$ (3 mols.)]; *Cu^{II} bisoxamidedioxime chloride*, $2RH_2$,$CuCl_2$ [from (**I**) (2 mols.) and $CuCl_2$ (1 mol.)] and *sulphate*; *Hg^{II} oxamidedioxime monochloride*, HgCl·RH; *Co^{III} bisoxamidedioxime chloride*, $2RH_2$,$CoCl_2$ [from (**I**) (2 mols.) and $CoCl_2$ (1 mol.) in $COMe_2$], and its *hexahydrate* (prepared in H_2O), which loses $6H_2O$ at 110°. Air passed through (**I**) (2 mols.), aq. $CoCl_2$ (1 mol.), and the respective base gives *di-amino-*, *-pyridino-*, *-ethylamino-*, and *-isoquinolino-dioxamidedioximecobaltic chloride*, $[Co(RH)_2(Base)_2]Cl$, respectively. A. T. P.

Detoxication. X. Characterisation of *p*-sulphonamidophenylglycuronide. H. G. Sammons, J. Shelswell, and R. T. Williams (*Biochem. J.*, 1941, **35**, 557—563).—The compound is characterised as 2 : 3 : 4-*trimethyl*-p-*sulphondimethylamidophenyl*-β-d-*glycuronamide*, m.p. 154—155°, $[\alpha]_D^{21}$ −42·3° in EtOH, $[\alpha]_D^{20}$ −52·2° in H_2O (*Me* ester, $[\alpha]_D^{27}$ −51·3° in $CHCl_3$; obtained by methylation of *Ba* p-*sulphonamidophenylglycuronate*, $[\alpha]_D$ −50° in H_2O). p-*Acetoxybenzenesulphonamide*, m.p. 158°, *veratrole-4-sulphondimethylamide*, m.p. 105°, and *pyrocatechol*-p-*sulphonanilide*, m.p. 221°, are incidentally reported. (See also A., 1941, III, 784.) H. W.

Conjugation and oxidation of *p*-hydroxybenzenesulphonamide in the rabbit.—See A., 1941, III, 784.

Unsaturated silico-organic compounds. Preparation of hexa-acetylenylsiloxan and triethoxyphenylacetylenylsilan. J. Volnov and A. Reutt (*J. Gen. Chem. Russ.*, 1940, **10**, 1600—1604).—CH:C·MgBr and $SiCl_4$ in Et_2O (12 hr. at room temp., then 3 hr. at the b.p.) yield *hexa-acetylenylsiloxan*, $[Si(C:CH)_3]_2O$, m.p. 19—20° (Ag_6 salt). CPh:C·MgBr and $Si(OEt)_4$ in xylene (3 hr. at 100°) afford *triethoxyphenylacetylenylsilan* (**I**), CPh:C·$Si(OEt)_3$, b.p. 141—142°/6 mm., and *diethoxydiphenyldiacetylenylsilan*, $(CPh:C)_2Si(OEt)_2$, b.p. 180—190°/12—13 mm. (**I**) is hydrolysed by boiling H_2O, as follows: (**I**) + $4H_2O$ → 3EtOH + CPh:CH + $Si(OH)_4$. R. T.

Reaction of Grignard reagents with silicofluorides. E. M. Soschestvenskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 1689—1693).—The yield of SiR_4 obtained from MgRX (R = Et, CH_2Ph, Ph; X = Cl, Br) and Na_2SiF_6 is unaffected by raising the reaction temp. or by conducting the reaction in H_2. It is increased by raising the ratio Na_2SiF_6 : MgRX from 1 : 4 to 4 : 1. R. T.

Metallo-organic compounds. X. Electroisomerism in tin triethyl. T. Harada (*Bull. Chem. Soc. Japan*, 1940, **15**, 481—483).—$SnEt_3$, prepared by the reduction of $SnEt_3$ halide (cf. Harada, A., 1939, II, 251) and oxidation of $SnEt_3Na$ (cf. Harada, A., 1930, 200), is assigned the electroisomeric constitutions $Sn^{+++}R^-_3$ and $Sn^{++}R^-_2R^+$, respectively, because when kept in contact with H_2O or 75% EtOH they are hydrolysed to $SnEt_2O$ to different extents, the latter about 3 times as much as the former in equal times. J. L. D.

II.—HOMOCYCLIC.

Silk oak flowers as source of β-carotene.—See A., 1941, III, 819.

Molecular volume of saturated hydrocarbons.—See A., 1941, I, 364.

Calculation of the boiling points of aromatic hydrocarbons.—See A., 1941, **I**, 369.

Multimolecular solvolysis: catalysis of racemisation and hydrolysis of optically active α-phenylethyl halides by polyhalide metallic salts.—See A., 1941, I, 381.

Polymerising action of methyl sulphate on ethylenic compounds. I. Polymerisation of αα-diphenylethylene. V. N. Belov and B. M. Lebedev (*J. Gen. Chem. Russ.*, 1940, **10**, 1543—1546).—$CPh_2:CH_2$ and Me_2SO_4 at 100° for 2 hr. yield $CPh_2:CH·CPh_2Me$, which is converted into 1 : 1 : 3-triphenyl-3-methylhydrindene when heated for 6 hr. with Me_2SO_4. R. T.

Preparation of α-chloro-αββ-triphenylethylene. J. van de Kamp and M. Sletzinger (*J. Amer. Chem. Soc.*, 1941, **63**, 1879—1881).—$CH_2Ph·CPh_2·OH$ with $KHSO_4$ at 155—160° or in boiling AcOH gives $CHPh:CPh_2$ (91·5, 90%), m.p. 67—68°, which with Cl_2 in AcOH at 30—40°, and then heating to remove HCl, gives 87·3% (over-all) of $CPh_2:CPhCl$, m.p. 117·5—118·5°. Contrary to Bergmann *et al.* (A., 1931, 947), $CHPh_2·COPh$ and PCl_5 in C_6H_6 give *αβ-dichlorotriphenylethane* (**I**) (49%), m.p. 110·5—111·5°, which in boiling MeOH gives *α-chloro-β-methoxy-αββ-triphenylethane*, m.p. 117·5—118°, in boiling abs. EtOH or at > the m.p. gives $CPh_2:CPhCl$, and is unchanged in boiling C_6H_6. $CHPh:CCl_2$ and PCl_5–C_6H_6 or Cl_2 give (**I**). R. S. C.

Alkyl-substituted hexa-arylethanes. XI. Symmetry and steric effects as factors in dissociation. C. S. Marvel, J. F. Kaplan, and C. M. Himel (*J. Amer. Chem. Soc.*, 1941, **63**, 1892—1896; cf. A., 1940, II, 302).—Dissociation of hexa-arylethanes is greatly increased by *o*-substituents, less so by symmetry, still less by *m*-, and least by *p*-substituents. Crude *o*-$C_6H_4Br·CH:CH_2$ and H_2–PtO_2 in C_6H_6 give *o*-C_6H_4EtBr, b.p. 86—88°/18 mm. [D. G. Botteron] *m*-$C_6H_4Br·CHO$ and $MgBu^{\alpha}Br$ give crude *m*-$C_6H_4Br·CHBu^{\alpha}·OH$, dehydrated by $KHSO_4$ to *m*-$C_6H_4Br·CH:CHPr^{\alpha}$, b.p. 142—145°/20 mm., which with H_2–PtO_2 in EtOH gives *m-bromo*-n-*amylbenzene*, b.p. 127—131°/16 mm. CPhMeEt$_2$, Br, and Fe powder give

p-C_6H_4Br·CMeEt$_2$, b.p. 123—125°/20 mm. *p*-C_6H_4Me·COCl, PhEt, and $AlCl_3$ give p-*tolyl* p-C_6H_4Et *ketone*, b.p. 196—198°/5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 166—167°). The following are prepared by Grignard reactions (sometimes "forced") and treatment of the resultant (usually oily) carbinols with warm AcCl: *phenyldi*-p-, m.p. 108—109°, -m-, m.p. 59—61° (*carbinol*, m.p. 81—82°), and -o-*tolylmethyl chloride*, m.p. 92—94° (*carbinol*, m.p. 81—82°); *diphenyl*-o-*ethyl*-, m.p. 87—88° (*carbinol*, m.p. 77—77·5°), -p-n-*propyl*-m.p. 90—91°, -p-iso*butyl*-, m.p. 79—80°, -p-sec.-*butyl*-, m.p. 84—85°, -p-tert.-*amyl*-, m.p. 90—91°, and -m-n-*amyl*-, m.p. 54—55°, -*phenylmethylchloride*; *phenyldi*-p-iso*propyl*-, m.p. 120—121°, -p-sec.-*butyl*-, m.p. 94—95°, -p-tert.-*butyl*-, m.p. 162—163°, and -tert.-*amyl*-, m.p. 98—99°, -*phenylmethyl chloride*; *tri*-p-tert.-*butyl*-, m.p. 259—260° (*carbinol*, m.p. 212—213°), and -tert.-*amyl-phenylmethyl chloride*, m.p. 160—161°; *phenyl*-p-*tolyl*-p-*ethyl*-, m.p. 107—108°, and -p-tert.-*butyl-phenylmethyl chloride*, m.p. 120—121°; *di*-p-*tolyl*-p-tert.-*amylphenylmethyl chloride*, m.p. 147—148°; p-*tolyldi*-p-tert.-*butylphenyl*-, m.p. 192—193° (*carbinol*, m.p. 141—142°), and p-*tolyl*-p-*ethylphenyl*-p-iso*propylphenyl-methyl chloride*, hygroscopic, m.p. 104—105°. The following (all symmetrical) are prepared therefrom by "mol." Ag in C_6H_6; percentages given refer to dissociation in C_6H_6, determined by magnetic susceptibility; figures in parentheses are m.p. of the derived *peroxides*: tetraphenyldi-*m*-tolylethane 6·5% (m.p. 154—155°); tetraphenyldi-*o*-ethyl- 33·0% (m.p. 140—141°), -p-n-*propyl*- 6·5% (m.p. 135—136°), -*p*-*iso*butyl- 7·5% (m.p. 121—122°), -*p*-*sec.*-butyl- 7·5% (m.p. 135—136°), -*p*-*tert.*-butyl- 7·5% (lit. 8—9%), -*p*-*tert.*-amyl- 8·0% (m.p. 147—148°), and -*m*-*n*-amyl- 9·0% (m.p. 102—103°), -phenylethane; diphenyltetra-*p*-tolyl- 5·5% (m.p. 139—140°), -*m*-tolyl- 7·0% (m.p. 152—153°), -*o*-tolyl- 82·0% (no peroxide), -*p*-*iso*propylphenyl- 8·0% (m.p. 140—141°), -*p*-*sec.*-butylphenyl- 8·5% (m.p. 130—131°), -*p*-*tert.*-butylphenyl- 8·5% (m.p. 177—178°), and -*p*-*tert.*-amylphenyl-ethane 9·0% (m.p. 151—152°); hexa-*p*-*n*-butyl- 20·0%, -*p*-*tert.*-butyl- 43·0% (m.p. 160—161°), and -*p*-*tert.*-amyl-phenylethane 40·0% (m.p. 162—163°); diphenyldi-*p*-tolyldi-*p*-ethyl- 6·0% (m.p. 93—94°) and -*p*-*tert.*-butyl-phenylethane 6·5% (m.p. 143—144°); tetra-*p*-tolyldi-*p*-*tert.*-butyl- 5·0% (m.p. 174—175°), di-*p*-tolyltetra-*p*-*tert.*-butyl- 5·0% (m.p. 175—176°), and di-*p*-tolyldi-*p*-ethylphenyldi-*p*-*iso*propyl-phenylethane 10·0% (no peroxide). *Phenyldi*-o-*tolylcarbinyl Et ether*, m.p. 99·5—100°, is obtained from the carbinol by EtOH and a drop of H_2SO_4. R. S. C.

Preparation of *sec.* amines. J. S. Buck and R. Baltzly (*J. Amer. Chem. Soc.*, 1941, **63**, 1964—1966).—Dialkylamines are prepared by the reactions, PhCHO + NH_2R → CHPh:NR → (H_2–PtO_2; AcOH; room temp.) CH_2Ph·NHR → CH_2Ph·NRR′ → (H_2–PtO_2–AcOH, 65—75°/3 atm.; less well, Pd–C–AcOH or Raney Ni–EtOH) NHRR′ + PhMe (or methyl*cyclo*hexane). The following are described. Benzylmethylethyl-, b.p. 80°/16 mm. (hydrochloride, m.p. 151—152°), -methyl-*n*-propyl-, b.p. 96—98°/15 mm., -*methyl*-n-*butyl*-, b.p. 113°/16 mm., -*methyl*-n-*amyl*-, b.p. 126°/15 mm., -methyl-*n*-dodecyl- (*hydrochloride*, m.p. 133—134°), -ethyl-*n*-propyl- (hydrobromide, m.p. 162°), -ethyl-*n*-butyl-, b.p. 115—116°/12 mm., -ethyl-*n*-amyl-, b.p. 117—121°/8 mm., -n-*propyl*-n-*butyl*-, b.p. 117°/8 mm. (*hydriodide*, m.p. 172°), and -*n*-butyl-*n*-amyl-amine, b.p. 145—146°/9 mm. N-*α-Naphthyl*-N′-*methyl*-N′-*ethyl*-, m.p. 129—130°, -n-*propyl*-, m.p. 108°, -n-*butyl*-, m.p. 88·5—89·5°, -n-*amyl*-, m.p. 73·5—75°, -n-*dodecyl*-, m.p. 74°, -N′-*ethyl*-N′-n-*propyl*-, m.p. 123—124°, -n-*butyl*-, m.p. 125—126°, -n-*amyl*-, m.p. 97°, -N′-n-*propyl*-N′-n-*butyl*-, m.p. 140°, and -N′-n-*butyl*-N′-n-*amyl*-, m.p. 117°, -*thiocarbamide*. M.p. are corr. R. S. C.

[Preparation of] methylanilines by demethylation of dimethylanilines. W. S. Emerson (*J. Amer. Chem. Soc.*, 1941, **63**, 2023—2024).—2 : 4 : 6 : 1-$C_6H_2R_3$·NMe_2 (R = Br, Cl, or Me) with aq. $NaNO_2$–HCl at 0° gives quantitatively $C_6H_2R_3$·NMe·NO, whence 2 : 4 : 6 : 1-$C_6H_2R_3$·NHMe is readily obtained. 2 : 4 : 6-*Tri-bromo*-, m.p. 91·5—92°, and -*chloro*-N-*nitroso*-N-*methylaniline*, m.p. 66·5—67°, 2 : 4 : 6 : 1-$C_6H_2Cl_3$·NMe_2, b.p. 128—138°/20 mm. (*perbromide*, m.p. 112—113°), and -$C_6H_2Me_3$·NMe·SO_2·C_6H_4Me-*p*, m.p. 147—147·5° (lit. 145—146°), are described. R. S. C.

Catalytic production of arylnaphthylamines.—See B., 1941, II, 297.

Derivatives of N^1-phenylsulphanilamide. II. G. L. Webster and S. D. Gershon (*J. Amer. Chem. Soc.*, 1941, **63**, 1927—1929; cf. A., 1938, II, 358).—2 : 4 : 1-NO_2·C_6H_3(NHAc)·OH and H_2–PtO_2 in hot EtOH give 2 : 4 : 1-NH_2·C_6H_3(NHAc)·OH, decomp. 221—222° (lit. 248°, 249°). 2 : 4 : 1-$(NHAc)_2C_6H_3$·OAc has m.p. 184—185° (lit. 180—182°). 3-*Amino*-4-*acetamidophenol*, m.p. 191°, is obtained from the *ON*^{4}-Ac_2 derivative by cold aq. NaOH and gives the *N*^{3}*N*^{4}-Ac_2, m.p. 212° (lit. 214—215°), and *N*^{3}*N*^{4}*O*-Ac_3 compound, m.p. 185—186° (lit. 187—188°). The following are prepared by standard procedures or slight modifications thereof. N^1-3′-*Nitro*-4′-*hydroxy*-, decomp. 189° (N^4-*Ac* derivative, decomp. 236°), N^1-3′-*amino*-4′-*hydroxy*-, decomp. 204°, N^1-2′-*amino*-5′-*hydroxy*-, decomp. 205° [N^{4}N^2′O-Ac_3, m.p. (+H_2O) 141—143°, (anhyd.) 200—201°, and N^{4}N^2′-Ac_2 derivative, decomp. 239—240°], N^1-3′-*nitro*-4′-*amino*-, decomp. 223—224° (N^4-*Ac* derivative, m.p. 258—259°), N^1-3′ : 4′-*diamino*-, decomp. 208—209° (N^4-*Ac* derivative, decomp. 230—231°), and N^1-5′-*amino*-2′-*hydroxy*-, decomp. 167—168° (N^{4}N^5′-Ac_2 derivative, decomp. 239—240°), -*phenylsulphanilamide*. N^4-*Acetyl*-N^1-2′-*nitro*-4′-*hydroxy*-, decomp. 217°, -4′-*nitro*-2′-*hydroxy*-, decomp. 222—223°, and -2′ : 5′-*diacetamido*-, decomp. 227—228°, -*phenylsulphanilamide*. N^{1}N^4-*Diacetyl*-N^1-3′-*nitro*-4′-*acetoxyphenylsulphanilamide*, decomp. 191°. 3-*Nitro*-4-*amino*-, decomp. 231—232° (*Ac* derivative, decomp. 211—212°), 5-*nitro*-2-*amino*-, decomp. 212° (*Ac* derivative, decomp. 217—217·5°), and 2 : 5-*diamino*-, decomp. 159—160° (Ac_2 derivative, decomp. 268°), -*phenyl* N-*acetylsulphanilate*. 3-*Nitro*-4-, decomp. 166·5—167·5°, and 5-*nitro*-2-*aminophenyl sulphanilate*, decomp. 217—218°. R. S. C.

Alkylation of phenylhydrazine in liquid ammonia. L. F. Audrieth, J. R. Weisiger, and H. E. Carter (*J. Org. Chem.*, 1941, **6**, 417—420).—Alkali-metal derivatives of NHPh·NH_2 (**I**) are readily obtained by the direct action of (**I**) in liquid NH_3 on the alkali metal or alkamide, the latter being preferable to avoid reduction. The compounds and the alkyl halides are sol. in liquid NH_3, thus facilitating complete reaction. The prep. of *N*-phenyl-*N*-benzyl-, -*N*-ethyl-, and -*N*-propyl-hydrazine (*CHPh:*, m.p. 64°, and p-*nitrobenzoyl* derivative, m.p. 153—154°) is described. Cleavage of the N·N linking in primary and unsymmetrically disubstituted hydrazines occurs in liquid NH_3 if an excess of Na is employed. H. W.

Bromination of *o*-diphenylyl acetate. S. E. Hazlet and H. A. Kornberg (*J. Amer. Chem. Soc.*, 1941, **63**, 1890—1892; cf. A., 1940, II, 12).—*o*-C_6H_4Ph·OAc and Br–AcOH give 5-*bromo*- (**I**), m.p. 65—66°, and 3 : 5-*dibromo*-2-*diphenylyl acetate* (**II**), m.p. 73—74°. (**I**) is also obtained from 2 : 4 : 1-C_6H_3PhBr·OH by Ac_2O–NaOAc and is hydrolysed by 20% NaOH thereto. (**II**) is similarly obtained from and hydrolysed to 2 : 4 : 6 : 1-$C_6H_2PhBr_2$·OH. 3 : 5-*Dibromo*-2-*diphenylyloxyacetic acid* has m.p. 123—124°. R. S. C.

Cyclic dehydration of diphenyl derivatives to fluorenes. (Miss) M. Anchel and A. H. Blatt (*J. Amer. Chem. Soc.*, 1941, **63**, 1948—1952).—The substance, m.p. 110°, obtained from 2 : 2 : 5″-trimethyldibenzpyran (Cahn, A., 1933, 1302) by HCl–AcOH and considered to be 1 : 5 : 2-C_6H_3PhMe·OH (**I**) (cf. Sherwood *et al.*, A., 1932, 843), is shown to be 4-*hydroxy*-1 : 9 : 9-*trimethylfluorene* (**II**). Its absorption spectrum resembles that of fluorenes and not that of (**I**). Its composition is confirmed by analyses of the Me ether (**III**), *Br*-, m.p. 123—124°, NO_2-, m.p. 136°, and PhN_2-derivative, m.p. 119·5—120·5°. With aq. $KMnO_4$, (**II**) gives *o*-CO_2H·C_6H_4·CMe_2·CO_2H, but (**III**) gives also 4-*methoxy*-9 : 9-*dimethylfluorene*-1-*carboxylic acid*, m.p. 233—234°, which in boiling HI gives 4-*hydroxy*-9 : 9-*dimethylfluorene* (**IV**), m.p. 90—91°. Formation of dibenzpyran from 2′-hydroxy-2-diphenylyldialkylcarbinol is reversible: HCl–AcOH at 200° converts 2′-hydroxy- and 2′-hydroxy-5′-methyl-2-diphenylyldimethylcarbinol into (**IV**) and (**II**), respectively. Formation of (**II**) in Cahn's reaction proceeds by way of the carbinol. (**I**) is prepared from cresidine by a diazo-reaction by way of 2-*methoxy*-5-*methyldiphenyl*, b.p. 150—155°/16 mm., and from PhN_2·HSO_4 and *p*-cresol at 70—100°, and is characterised by an *acetate*, m.p. 28—29°, and *benzoate*, m.p. 94—94·5°. 1 : 5 : 2-C_6H_3PhMe·OMe and $KMnO_4$ give 2 : 1 : 5-OMe·C_6H_3Ph·CO_2H, also obtained from *o*-C_6H_4Ph·OAc by Fries rearrangement, methylation, and oxidation. *o*-C_6H_4Ph·CO_2Me and MgRHal give o-*diphenylyl-dimethyl*-, m.p. 73°, and -*dibenzyl-carbinol*, m.p. 98—98·5°, converted by conc. H_2SO_4 into 9 : 9-dimethyl- (also obtained by HCl–AcOH) and -dibenzyl-fluorene, respectively. R. S. C.

Removal of acyl groups. R. Baltzly and J. S. Buck (*J. Amer. Chem. Soc.*, 1941, **63**, 2022—2023).—*o*-$C_6H_4(OAc)_2$, β-$C_{10}H_7$·OAc, $C(CH_2·OAc)_4$, and *p*-$C_6H_4(O·COEt)_2$ (0·01 mol.) are hydrolysed by 38% (wt./wt.) HCl–EtOH (0·5 g.) in MeOH (35—50 c.c.) at room temp. for 24 hr. α-$C_{10}H_7$·OAc is less readily hydrolysed; Bz and CO_2Et groups react still more slowly. R. S. C.

Vitamin-*E*. XXX. Condensation of butadiene and of crotyl systems with trimethylquinol. L. I. Smith and J. A. King (*J. Amer. Chem. Soc.*, 1941, **63**, 1887—1890; cf. A., 1941, I, 270).—2 : 3 : 5 : 1 : 4-$C_6HMe_3(OH)_2$ (**I**), $Zn(CN)_2$, HCl, and $AlCl_3$ give 2 : 5-*dihydroxy*-3 : 4 : 6-*trimethylbenzaldehyde*, m.p. 146—147° [*semicarbazone*, m.p. 234—235° (decomp.)], which in an attempted condensation with COMe·CH_2Cl regenerated (**I**). CHMe:CH·CH_2·OH, (**I**), and $ZnCl_2$ at 100° give 2 : 3 : 5-*trimethyl*-6-*crotylquinol* (**II**), m.p. 143·5—144·5°, which gives no Furter–Meyer reaction, is cyclised by HBr–AcOH to 5-hydroxy-4 : 6 : 7-trimethyl-2-ethylcoumaran (**III**), m.p. 123—124°, and converted by $AgNO_3$–EtOH into the quinone, which with Zn dust–NaOAc–Ac_2O gives the *diacetate*, m.p. 83—84° (*dibromide*, m.p. 148—148·5°), of (**II**), also obtained directly. The Me_2 *ether*, b.p. 150°/10 mm., of (**II**) and O_3 give 2 : 5 : 3 : 4 : 6 : 1-$(OMe)_2C_6Me_3·CH_2·CO_2H$. $(CH_2:CH)_2$, (**I**), $ZnCl_2$, and H_2SO_4 (2 drops) in AcOH also give (**II**). CHMe:CH·CH_2Cl gives (**III**) owing to the cyclising effect of the HCl evolved. CHMe:CH·CH_2Br gives a mixture of (**III**) and the isomeric chroman owing to this cyclising and the peroxide effects. CH_2:CH·CHMe·OH or CH_2:CH·CHMeCl with (**I**) gives (**II**) (cf. A., 1940, II, 20). R. S. C.

Halogenation of phenolic ethers and anilides. XI. Substituted benzyl ethers of some alkylphenols. B. Jones (*J.C.S.*, 1941, 358—364; cf. A., 1941, II, 221).—Comparative velocity coeffs. for the chlorination in 99% AcOH at 20° of 1 : 3 : 4-C_6H_3AlkBr·OR [Alk = Et, R = *p*-$C_6H_4Y·CH_2$ (Y = Me, Cl, NO_2) and *m*-$NO_2·C_6H_4·CH_2$; Alk = Pr$^\alpha$, R = *o*-, *m*-, and *p*-$NO_2·C_6H_4·CH_2$; Alk = Bu$^\gamma$, R = CH_2Ph, *p*-$C_6H_4Y·CH_2$ (Y = Me, Cl, Br, NO_2), and *m*-$NO_2·C_6H_4·CH_2$; Alk = CMe_2Et, R = CH_2Ph, *p*-$C_6H_4Y·CH_2$ (Y = Me, Cl, NO_2) and *m*-$NO_2·C_6H_4·CH_2$], 3 : 1 : 4-$NO_2·C_6H_3Bu^\gamma$·OR (R = CH_2Ph, *p*-$C_6H_4Br·CH_2$), and (in 99% AcOH at 20° and 99·5% AcOH at 16°) 1 : 4 : 2 : 5-$C_6H_2MePr^\beta X$·OR [X = Cl, R = CH_2Ph, *p*-$C_6H_4Y·CH_2$ (Y = Me, Cl, Br), *o*-$NO_2·C_6H_4·CH_2$; X = Br, R = CH_2Ph, *p*-$C_6H_4Cl·CH_2$, *o*-$NO_2·C_6H_4·CH_2$] are recorded. In all cases, the relative directive powers of the various ·O·CH_2Ph groups are the same as in the simpler ethers of type *p*-$C_6H_4X·OR$ (X = Cl, Br, F, CO_2H). The presence of Me and Pr$^\beta$ in the 6-halogenothymol ethers increases the rate of chlorination 212 times as compared with those of the *p*-halogenophenyl ethers. For analogous ethers with varying alkyl groups, the relative velocities of substitution are Me : Et : Pr$^\alpha$: Bu$^\gamma$: CMe_2Et = 100 : 121 : 92·5 : 48·5 : 40·5 (this series represents a deviation from the theoretical sequence required by operation of their general inductive effects) (cf. Hughes *et al.*, A., 1940, I, 391). The following ethers are described: 1 : 3 : 4-C_6H_3EtBr·OR (R = p-*methyl*-, m.p. 36°, p-*chloro*-, m.p. 29°, o-, m.p. 97°, m-, m.p. 86°, and p-*nitrobenzyl*, m.p. 81°), 1 : 3 : 4-$C_6H_3Pr^\alpha$Br·OR (R = o-, m.p. 64°, m-, m.p. 67°, and p-*nitrobenzyl*, m.p. 76°), 1 : 3 : 4-$C_6H_3Bu^\gamma$Br·OR (R = *benzyl*, m.p. 29°, b.p. 225°/19 mm., p-*methyl*-, m.p. 49°, p-*chloro*-, m.p. 73°, p-*bromo*-, m.p. 78°, m-, m.p. 75°, and p-*nitro-benzyl*, m.p. 94°), 1 : 3 : 4-$CMe_2Et·C_6H_3Br·OR$ (R = *benzyl*, b.p. 234°/19 mm., m.p. 44°, p-*methyl*-, m.p. 49°, p-*chloro*-, m.p. 86°, and o-, m.p. 64°, m-, m.p. 68°, and p-*nitro-benzyl*, m.p. 82°), 3 : 1 : 4-$NO_2·C_6H_3Bu^\gamma$·OR (R = *benzyl*, m.p. 53°, and p-*bromobenzyl*, m.p. 66°), 1 : 4 : 2 : 5-$C_6H_2MePr^\beta Cl$·OR (R = *benzyl*, m.p. 55°, p-*methyl*-, m.p. 51°, p-*chloro*-, m.p. 59°, p-*bromo*-, m.p. 69°, and o-*nitro-benzyl*, m.p. 117°), and 1 : 4 : 2 : 5-$C_6H_2MePr^\beta Br$·OR (R = *benzyl*, m.p. 51°, p-*chloro*-, m.p. 60°, and o-*nitro-benzyl*, m.p. 116°). A. T. P.

Ethers of duroquinol and trimethylquinol.—See B., 1941, III, 244.

Formation of solid derivatives of amines. II. J. H. Billman, J. Garrison, R. Anderson, and B. Wolnak (*J. Amer. Chem. Soc.*, 1941, **63**, 1920—1921; cf. A., 1939, II, 500).—2 : 4 : 1-$(NO_2)_2C_6H_3$·SCl (prep. from the disulphide by Cl_2), m.p. 94—96°, and NH_2R in Et_2O or 30% aq. solution at room temp. give 2 : 4-*dinitrobenzenesulphen-anilide*, m.p. 142·5—143°, -p-*anisidide*, m.p. 158—159°, -p-*bromoanilide*, m.p. 180·5—181°, -n-*butylamide*, m.p. 88·5—89°, -p-*chloroanilide*, m.p. 164—164·5°, -cyclo*hexylamide*, m.p. 109·5—110°, *-ethylamide*, m.p. 66—66·5°, *-methylamide*, m.p. 99—99·5°, -cyclo*hexyl*-N-*methylamide*, m.p. 95·5—96°, -α-, m.p. 188·5—189°, and -β-*naphthylamide*, m.p. 167—168°, -n-*propylamide*, m.p. 94—94·5°, -o-, m.p. 155—156°, and -p-*toluidide*, m.p. 161—161·5°, which with HCl–Et_2O regenerate NH_2R. R. S. C.

Electrochemical introduction of the thiocyanate radical into organic compounds. II. Aromatic amines. E. M. Tscherkasova, S. I. Skljarenko, and N. N. Melnikov (*J. Gen. Chem. Russ.*, 1940, **10**, 1373—1376).—The following compounds were prepared (A., 1940, II, 169) by electrolysis of solutions in aq. EtOH–HCl of amines: 4-*thiocyano*-N-*methyl*-, m.p. 43—44°, *-propyl*-, b.p. 156—162°/2 mm., and *-butyl-aniline*, b.p. 170°/2 mm., 6-*thiocyano*-N-*ethyl*-m-*toluidine*, m.p. 63·5—64·5°, 5-thiocyanoanthranilic acid and its N-*M* derivative, m.p. 201—202°. R. T.

Friedel–Crafts reactions with halides containing sulphur. I. Synthesis of 4 : 4′-diaminodiphenyl sulphone. S. Sugasawa and K. Sakurai (*J. Pharm. Soc. Japan*, 1940, **60**, 1—3).—Addition of $AlCl_3$ (2·2) to NHPhAc (10·8) and $SOCl_2$ (4·8 g.) in boiling CS_2 (120 c.c.) (not in $C_2H_2Cl_4$ at 60—70°) gives 80% of (*p*-NHAc·$C_6H_4)_2$SO, m.p. 278°, oxidised by $K_2Cr_2O_7$–H_2SO_4 to (*p*-NHAc·$C_6H_4)_2SO_2$, m.p. 283°, which in boiling 10% HCl gives (*p*-$NH_2·C_6H_4)_2SO_2$, m.p. 176° [(*p*-*NHAc*·C_6H_4·$SO_2)_2$ derivative, m.p. 273—274°]. NHPhAc, $AlCl_3$, and SO_2Cl_2 under varying conditions give only *p*-$C_6H_4Cl·NHAc$. R. S. C.

Chemotherapy. III. Sulphones. R. O. Roblin, jun., J. H. Williams, and G. W. Anderson (*J. Amer. Chem. Soc.*, 1941, **63**, 1930—1934; cf. A., 1940, **II**, 359).—The following are prepared, essentially by condensing *p*-NHAc·$C_6H_4·SO_2Na$ with a reactive halogen compound and hydrolysing the product. Chemotherapeutic activity (strepto- or pneumo-cocci; white mice) is indicated in parentheses as follows: *A* = active; *S* = slightly active; *I* = inactive. (*p*-$NH_2·C_6H_4)_2SO_2$ (*A*), m.p. 175° [Ac_1 derivative (*A*), m.p. 242—243°]. 4-*Amino*-4′-*octanesulphonamido*- (*I*), m.p. 130°, and -4′-*sulphanilamidodiphenyl sulphone* (*A*), m.p. 211°. 4 : 4′-*Diamino*-2-*sulphamyl*- (*A*), *forms*, m.p. 238° (slight decomp.) and 222—224° (decomp.), -2-*carboxy*- (*I*), +1·5EtOH, m.p. 108—113°, and -2-*carbethoxy-diphenyl sulphone* (*I*), m.p. 182—183°. 2 : 4′-*Diamino*- (*I*), m.p. 117°, 2-*nitro*-4′-*amino*-4-*sulphamyl*- (*S*), m.p. 223—225°, 2 : 4′-*diamino*-4-*sulphamyl*- (*I*), m.p. 206—207°, and 4-amino- (*S*), m.p. 176°, -diphenyl sulphone. p-*Aminophenyl* 2- (*A*), m.p. 158—160°, and 4-*pyridyl* (*I*), m.p. 269—271°, 2-*thiazolyl* (*I*), m.p. 149—151°, 5-*nitro*-2-*pyridyl* (*S*), m.p. 169—171°, and 5-*amino*-2-*pyridyl* (*A*), m.p. 186—187°, *sulphone*. Relations between activity and structure in the sulphone and sulphonamide series are discussed. M.p. are corr. R. S. C.

Hydrogen fluoride as condensing agent. XV. Preparation of esters and ethers. J. H. Simons and A. C. Meunier (*J. Amer. Chem. Soc.*, 1941, **63**, 1921—1922; cf. A., 1941, II, 164).—At 0°/1 atm. *cyclo*hexene (**I**) and Δ^α- + Δ^β-octene with AcOH or Pr$^\alpha CO_2H$ in HF give good yields of the *cyclo*hexyl and octyl esters, respectively, but CHMe:CMe_2 merely polymerises. HF also promotes formation and hydrolysis of EtOAc. *cyclo*Hexanol and (**I**) in HF give di*cyclo*hexyl ether (12%) with 61·5% of *cyclo*hexyl fluoride, but attempts to form other ethers failed. R. S. C.

Hydrogenation of polymeric acyloins [to *cyclo*alkane-1 : 2-diols].—See B., 1941, II, 298.

Preparation of glycerophenylose enediol diacetate. W. G. Dauben, W. L. Evans, and R. I. Meltzer (*J. Amer. Chem. Soc.*, 1941, **63**, 1883—1885).—COPh·CH_2Br (modified prep.) and KOAc in boiling Ac_2O gives *αβ-diacetoxystyrene* ["*glycerophenylose enediol diacetate*"], b.p. 118—120°/2 mm., the structure of which is proved by conversion by boiling KOAc–AcOH into $CH_2Bz·OAc$, by $CaCO_3$ in boiling H_2O into $CH_2Bz·OH$, by H_2–PtO_2 into OAc·CHPh·CH_2·OAc, and by $CuSO_4$–NaOH–H_2O at 100° into *dl*-OH·CHPh·CO_2H. R. S. C.

Preparation of amino-ketones and amino-alcohols containing the *ac*-tetrahydro-β-naphthylamine, tetrahydro*iso*quinoline, or β-phenylethylamine nucleus. A. L. Allewelt and A. R. Day (*J. Org. Chem.*, 1941, **6**, 384—400).—In the prep. of NH_2-ketones 2 equivs. of the amine are allowed to react with one equiv. of the ω-halogenoketone in dry EtOH or Et_2O;

after definite periods Et_2O is added and the pptd. amine hydrochloride is removed. Dry HCl is passed over the surface of the well-stirred filtrate with avoidance of excess of gas, whereby the ketone hydrochloride is pptd.; from it the free base is obtained by use of 5% $NaHCO_3$. The ketone hydrochlorides are catalytically reduced (10% Pd–C) to the NH_2-alcohols, the hydrochlorides of which are transformed by an excess of BzCl into the esters. The following are described: *ω-ac*-tetrahydro-*β*-naphthylaminoacetophenone, an oil (*hydrochloride*, m.p. 197—199°; *oxime*, m.p. 120°); *β*-ac-*tetrahydro*-2-*naphthylamino*-*α*-*phenylethanol*, m.p. 78·5° (*hydrochloride* (**I**), m.p. 212—213°; *benzoate*, m.p. 68·5° (*hydrochloride*, m.p. 174—175°)]; *α*-ac-*tetrahydro*-2-*naphthylaminopropiophenone*, unstable and hygroscopic, m.p. 40—41° [*hydrochloride*, m.p. 199—200° (decomp.); *oxime*, m.p. 137°]; *β*-ac-*tetrahydro*-2-*naphthylamino*-*α*-*phenylpropanol*, m.p. 69·5—70° [*hydrochloride* (**II**), m.p. 206—208°; *benzoate*, m.p. 58·5—59·5° (*hydrochloride*, m.p. 139·5—141°)]; *ω*-ac-*tetrahydro*-2-*naphthylamino*-2′-*acetonaphthone*, m.p. 84·5—85·5° [*hydrochloride*, m.p. 170° (decomp.); *oxime*, m.p. 145°]; *β*-ac-*tetrahydro*-2-*naphthylamino*-*α*-2′-*naphthylethanol*, m.p. 93·5° [*hydrochloride*, m.p. 211—212°; *benzoate*, m.p. 101·5° (*hydrochloride*, m.p. 201·5—203°)]; *β*-ac-*tetrahydro*-2-*naphthylamino*-*α*-*phenylethane hydrochloride*, m.p. 245—246·5°; *ω*-ac-*tetrahydro*-2-*naphthylamino*-p-*hydroxyacetophenone*, m.p. 117—118° (*hydrochloride*, m.p. 221°; an oxime or semicarbazone could not be prepared); *β*-ac-*tetrahydro*-2-*naphthylamino*-*α*-p-*hydroxyphenylethanol*, m.p. 173—175° [*hydrochloride* (**III**), m.p. 198—199·5°]; ac-*tetrahydro*-2-*naphthyl*-*β*-*phenoxyethylamine hydrochloride*, m.p. 226—228°; *ω*-tetrahydro*iso*quinolinoacetophenone, m.p. 63·5—64·5° (lit. 100—101°) (*hydrochloride*, m.p. 168—169°; *oxime*, m.p. 136·5°); *α*-*phenyl*-*β*-*tetrahydroisoquinolinoethanol*, m.p. 56·5—57° [*hydrochloride* (**IV**), m.p. 206—207°; *benzoate*, m.p. 98·5° (*hydrochloride*, m.p. 169·5—170·5°)]; *α*-*tetrahydroisoquinolinopropiophenone*, m.p. 38° (*hydrochloride*, m.p. 173—175°; *oxime*, m.p. 63°); *α*-*phenyl*-*β*-*tetrahydroisoquinolinopropanol*, m.p. 96·8—97·5° (*hydrochloride*, m.p. 235°; a Bz derivative could not be prepared); *ω*-*tetrahydroisoquinolino*-2-*acetonaphthone*, m.p. 71·5° (*hydrochloride*, m.p. 188—189·5°; *oxime*, m.p. 128°); *α*-2-*naphthyl*-*β*-*tetrahydroisoquinolinoethanol*, m.p. 91° [*hydrochloride*, m.p. 219—221°; *benzoate*, m.p. 112° (*hydrochloride*, m.p. 164·5—165°)]; *α*-*phenyl*-*β*-*tetrahydroisoquinolinoethane*, m.p. 43° [*hydrochloride* (**V**), m.p. 216—218°]; *ω*-*tetrahydroisoquinolino*-p-*hydroxyacetophenone*, m.p. 154° (*hydrochloride*, m.p. 216—217°; an oxime could not be obtained); *α*-p-*hydroxyphenyl*-*β*-*tetrahydroisoquinolinoethanol*, m.p. 156° [*hydrochloride* (**VI**), m.p. 217—219°]; N-*β*-*phenoxyethyltetrahydroisoquinoline*, m.p. 35° (*hydrochloride*, m.p. 180·5—182°); *ω*-*β*-phenylethylaminoacetophenone [*hydrochloride*, m.p. 175—177° (decomp.); *oxime*, m.p. 123°; the free base could not be isolated]; *β*-*β*′-*phenylethylamino*-*α*-*phenylethanol*, m.p. 89·5—90° [*hydrochloride*, m.p. 205—206°; *benzoate*, m.p. 101° (*hydrochloride*, m.p. 146·5—148°)]; *α*-*β*′-phenylethylaminopropiophenone, an impure oil [*hydrochloride*, m.p. 175—177° (decomp.); *oxime*, m.p. 152·5°]; *β*-*β*′-*phenylethylamino*-*α*-*phenylpropanol*, m.p. 101·5—102° [*hydrochloride*, m.p. 208—209°; *benzoate*, m.p. 93·5° (*hydrochloride*, m.p. 185°)]; *ω*-*β*-phenylethylamino-2-acetonaphthone [*hydrochloride*, m.p. 174—177° (decomp.); *oxime*, m.p. 123°]; *β*-*β*′-*phenylethylamino*-*α*-2-*naphthylethanol*, m.p. 59·5—60° [*hydrochloride*, m.p. 194—196°; *benzoate*, m.p. 111·5—112° (*hydrochloride*, m.p. 180·5—181·5°)]; *α*-*β*′-*phenylethylamino*-*β*-*phenoxyethane hydrochloride*, m.p. 230—231°. M.p. are corr. (**I**) and (**II**) in 0·5% solution produce anæsthesia of longer duration than did 1% cocaine solution on rabbit's cornea; (**III**) and (**IV**) are somewhat less efficient than cocaine whilst (**V**) and (**VI**) are inactive. H. W.

Marine products. VIII. Sterol of sponges; clionasterol and poriferasterol. F. R. Valentine, jun., and W. Bergmann (*J. Org. Chem.*, 1941, **6**, 452—461).—Clionasterol as isolated from the marine sponges *Spheciospongia vesparia* and *Cliona celata* is a mixture of a mono- (**I**) and a di-unsaturated sterol (**II**). For (**I**), $C_{29}H_{50}O$, which represents ~60% of the mixture, the name clionasterol is retained. (**II**), $C_{29}H_{48}O$, is designated *poriferasterol*. (**I**), m.p. 137·5—138·5°, $[\alpha]_D^{24}$ −37°, gives the Liebermann–Burchard and Salkowski reaction and resembles cholesterol in solubility. It gives an *acetate*, m.p. 137°, $[\alpha]_D^{24}$ −41·9°, *propionate*, m.p. 117—118°, $[\alpha]_D^{22}$ −41·84°, *benzoate*, m.p. 134·5—135°, $[\alpha]_D^{22}$ −16·8°, *phenylurethane*, m.p. 180·5—182°, $[\alpha]_D^{23}$ −29·36°, 3 : 5-*dinitrobenzoate*, m.p. 201—203°, $[\alpha]_D^{23}$ −13·95°, and o-*iodobenzoate*, m.p. 103·5—104·5°, $[\alpha]_D^{22}$ −19·76°. (**II**), m.p. 155—156°, $[\alpha]_D^{24}$ −49·7°, gives the Salkowski and Liebermann–Burchard reactions. The *acetate* (**III**), m.p. 146·5—147°, $[\alpha]_D^{24}$ −53·0°, gives a *dibromide*, m.p. 211—212° (decomp.) after darkening at 202°, $[\alpha]_D^{25}$ −31°, a *tetrabromide*, m.p. 185° (decomp.), $[\alpha]_D^{24}$ −43·5°, and absorbs 2 O from BzO_2H. (**II**) affords a *propionate*, m.p. 125—125·5°, $[\alpha]_D^{24}$ −48·1°, *benzoate*, m.p. 139·5—140·5° (turbid), 141·5° (clear), $[\alpha]_D^{24}$ −21·95°, *phenylurethane*, m.p. 191—192·5°, $[\alpha]_D^{24}$ −33·2°, 3 : 5-*dinitrobenzoate*, m.p. 227—228°, $[\alpha]_D^{24}$ −22·1°, and o-*iodobenzoate*, m.p. 153—154·5°, $[\alpha]_D^{24}$ −25·3°. Hydrogenation (PtO_2 in glacial AcOH at 60—70°) of (**III**) leads to *poriferastyl acetate*, $C_{31}H_{54}O_2$, m.p. 140—141°, $[\alpha]_D^{24}$ +16·3°, hydrolysed to *poriferastanol* (**IV**), m.p. 143—144°, $[\alpha]_D^{24}$ +247° (3 : 5-*dinitrobenzoate*, m.p. 213—213·5°, $[\alpha]_D^{24}$ +17·1°), which is oxidised (CrO_3 in 95% AcOH) to *poriferastanone*, $C_{29}H_{50}O$, m.p. 161—161·5°, $[\alpha]_D^{24}$ +46·7°. M.p. are corr. and $[\alpha]_D$ are in $CHCl_3$. (**IV**) closely resembles ostreastanol. H. W.

Separated auxo-enoid systems. XIII. Colour phenomena in 3 : 5-dinitrobenzoyl derivatives of aromatic amines, and the analogy of these compounds to molecular compounds. E. A. Smirnov (*J. Gen. Chem. Russ.*, 1940, **10**, 1377—1384).—The compounds $R{\cdot}CO{\cdot}NH{\cdot}C_6H_4R'$ [R = 3 : 5-dinitrophenyl, R′ = p-NMe_2, m.p. 282°, m-NMe_2, m.p. 241° (decomp.), p-*OH*, m.p. 267·5°, m-*OH*, m.p. 260° (decomp.), p-*OMe*, m.p. 238·5°, and m-*OMe*, m.p. 189·5°], and $R{\cdot}CO{\cdot}NH_2{\cdot}NHAc{\cdot}C_6H_4R'$ (R = 3 : 5-dinitrophenyl, R′ = p-NMe_2, m.p. 146°, m-NMe_2, m.p. 201°, p-*OH*, m.p. 171·5°, and m-*OH*, m.p. 212°) have been prepared by standard reactions. The colours of these two classes of compounds are similar, depending on the nature and position of R′, but are in general deeper for the mol. compounds than for the corresponding dinitrobenzanilides. The colour is in both cases due to interaction of the nitro-enoid with the auxo-enoid systems. 3 : 5-*Dinitrobenz*-p-*hydroxy*-N-*methylanilide*, m.p. 255°, has an intense yellow colour, showing that tautomerism of the type $\cdot CO{\cdot}NH\cdot \rightleftharpoons \cdot C(OH){:}N\cdot$ is not essential for possession of colour. R. T.

Effect of resonance or reaction velocity. F. H. Westheimer and R. P. Metcalf (*J. Amer. Chem. Soc.*, 1941, **63**, 1339—1343).—See A., 1941, I, 340. *p*-$NMe_2{\cdot}C_6H_4{\cdot}CO_2Et$, prepared from the acid, has m.p. 63—63·5° (< lit.). 1 : 3 : 5 : 2-$C_6H_2Me_2Br{\cdot}NH_2$ and Me_2SO_4 at 160° give 5-*bromo*-2-*dimethylamino*-m-*xylene*, m.p. 33° (*nitrosoamine*, $C_9H_{11}ON_2Br$, m.p. 69°), converted by Li in Et_2O and N_2 followed by CO_2 into 4-*dimethylamino*-3 : 5-*dimethylbenzoic acid*, m.p. 188° (*Et* ester, m.p. 15°), together with (?) 4 : 4′-*tetramethyldiamino*-3 : 5 : 3′ : 5′-*tetramethylbenzophenone*, m.p. 145°. 3 : 5 : 1-$C_6H_3Me_2{\cdot}CO_2H$ is obtained in >80% yield from 3 : 5 : 1-$C_6H_3Me_2Br$ by the Grignard reaction.

Chloralamides. VII. Reactivity of the α-hydroxy-group in chloralbromosalicylamides and their methyl ethers. N. W. Hirwe and B. V. Patil. **VIII. Condensation of toluamides with chloral. IX. Reactivity of α-chlorine atom in α-chlorochloraltoluamides.** N. W. Hirwe and J. S. Deshpande (*Proc. Indian Acad. Sci.*, 1941, **A, 13**, 273—274, 275—276, 277—280; cf. A., 1941, II, 13).—VII. The reactivity of the α-OH in chloral-3- and -5-bromo-salicylamide, -5-bromo- and -3 : 5-dibromo-2-methoxybenzamide, and -3 : 5-dibromosalicylamide is studied. Ac_2O in alkaline medium gives the anhydrocompound, whilst in acid medium it affords completely acetylated products. The following are described: *chloral*-3-, m.p. 119—120°, and -5-*bromo*-*α* : 2-*diacetoxybenzamide*, m.p. 151—152°; *chloral*-5-*bromo*-*α* : 2-*dimethoxy*-, m.p. 160°, and -*dibenzoyloxy*-*benzamide*, m.p. 97—100°; *chloral*-5-*bromo*-*α*-*acetoxy*-, m.p. 134—135°, and -*benzoyloxy*-2-*methoxybenzamide*, m.p. 145—146°; *anhydro*(*chloral*-5-*bromo*-2-*methoxybenzamide*), m.p. 149—150°; *chloral*-3 : 5-*dibromo*-*α* : 2-*diacetoxy*-, m.p. 155—157°, and -*dimethoxy*-*benzamide*, m.p. 108—109°; *chloral*-3 : 5-*dibromo*-*α*-*acetoxy*-, m.p. 117—119°, and -*benzoyloxy*-2-*methoxybenzamide*, m.p. 124—126°; *chloral*-3 : 5-*dibromo*-*α*-*methoxysalicylamide*, m.p. 176—177°; *α*-*anhydro*-(*chloral*-3 : 5-*dibromo*-2-*methoxybenzamide*), m.p. 136—137°.

VIII. Chloral condenses with $C_6H_4Me{\cdot}CO{\cdot}NH_2$ to *chloral*-o-*toluamide*, m.p. 151—153° [BzCl or Ac_2O in alkali gives some *anhydro*-compound, m.p. 219—220°; *α*-*Me*, m.p. 120—121°, *α*-*Ac*, m.p. 159—160° (formed in acid or alkali medium), and *α*-*Bz* derivative, m.p. 149—151°]; *chloral*-m-*toluamide*, m.p. 145° (BzCl in alkali affords the *anhydro*-compound, m.p. 165—167°, and a *product*, $C_{20}H_{16}O_2N_2Cl_6$, m.p. 150—152°; *α*-*Bz*,

m.p. 157—158°, and α-*Ac* derivative, m.p. 142°); chloral-*p*-toluamide, m.p. 151—152° (α-*Ac* derivative, m.p. 159—160°; BzCl in alkali yields the *anhydro*-compound, m.p. 200—202°, and a *substance*, m.p. 198—200°).

IX. The α-Cl in $C_6H_4Me{\cdot}CO{\cdot}NH{\cdot}CHCl{\cdot}CCl_3$ (**I**) is reactive. (**I**) (from the chloralamide and PCl_5) and $(NH_4)_2CO_3$ give the α-NH_2-compounds, whilst KCN (1 mol.) affords the impure α-CN-derivatives, and KCN (2 mols.) yields the vinyl compounds. The following are described: α-*chloro*-, m.p. 172—173°, -*methoxy*-, m.p. 121°, -*ethoxy*-, m.p. 127—128°, -*amino*-, m.p. 228—229°, -*anilino*-, m.p. 176—177°, -*methylanilino*-, m.p. 135—136°, and -*phenoxy-chloral*-o-*toluamide*, m.p. 146—147°; α-*chloro*-, m.p. 132—134°, -*methoxy*, m.p. 98°, -*ethoxy*-, m.p. 145—146°, -*amino*-, m.p. 208—210°, -*anilino*-, m.p. 166°, -o-*anisidino*-, m.p. 149°, -o-*phenetidino*-, m.p. 145°, -*phenoxy*-, m.p. 140—141°, and -o-*tolyloxy-chloral*-m-*toluamide*, m.p. 156°; N-ββ-*dichloro*-α-*cyano*-, m.p. 161°, and -*carboxy-vinyl*-m-*toluamide*, m.p. 189°; α-*chloro*-, m.p. 111°, -*methoxy*-, m.p. 112—113°, -*ethoxy*-, m.p. 116—117°, -*amino*-, m.p. 210°, -*anilino*-, m.p. 132°, -o-*toluidino*-, m.p. 153°, -*piperidino*-, m.p. 132, and -*phenoxy-chloral*-p-*toluamide*, m.p. 129—131°; N-ββ-*dichloro*-α-*cyano*-, m.p. 167°, and -*carboxy-vinyl*-p-*toluamide*, m.p. 180° [*Na* (+$2H_2O$) and *Ba* (+H_2O) salts]. A. T. P.

Antiseptic action of phenols, phenolcarboxylic acids, and their esters present in lichens. VIII. Esters of β-orcinolcarboxylic acid. F. Fuzikawa (*J. Pharm. Soc. Japan*, 1940, **60**, 177—178; cf. B., 1940, 565).—K diffractate and AlkI at 170° give the Et, m.p. 142°, *Pr*α, m.p. 127°, *Bu*α, m.p. 115°, *Bu*β, m.p. 114°, n-, m.p. 90°, and iso-*amyl* ester, m.p. 93°, converted by cold, conc. H_2SO_4 into rhizoninic acid Me ether and *Et*, m.p. 128°, *Pr*α, m.p. 139°, *Pr*β, m.p. 92°, *Bu*α, m.p. 123°, *Bu*β, m.p. 121°, n-, m.p. 117°, and iso-*amyl* β-*orcinolcarboxylate*, m.p. 108°. *Et*, m.p. 122°, *Pr*α, m.p. 94—95°, *Pr*β, m.p. 106°, *Bu*α, m.p. 90°, *Bu*β, m.p. 80°, n-, m.p. 58—59°, and iso-*amyl acetyldiffractate*, m.p. 88°, obtained from acetyldiffractic acid by Ag_2O and AlkI, with conc. H_2SO_4 give the same fission products. R. S. C.

Reaction of furoic acid with aromatic compounds. C. C. Price, E. C. Chapin, A. Goldman, E. Krebs, and H. M. Shafer (*J. Amer. Chem. Soc.*, 1941, **63**, 1857—1861).—Yields of α-$C_{10}H_7{\cdot}CO_2H$ (**I**) etc. obtained from 2-furoic acid (**II**) and C_6H_6 etc. are low (10—20%) owing to formation also of more complex products. (**II**) (best purified by way of an ester), C_6H_6, and $AlCl_3$ at 0° and then ~60° give (**I**) (7—10%), 1 : 4-*diphenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-1-*carboxylic acid* (**III**) (~60%), amorphous, softens 80—100° [converted by decarboxylation (Cu chromite–quinoline; 210—220°) and then dehydrogenation (S; 250—300°) into 1 : 4-$C_{10}H_6Ph_2$], and 9 : 10-*endo*ethylene-9 : 10-dihydroanthracene-9-carboxylic acid (**IV**) (~15%). Presence of (**IV**) is inferred from oxidation by $KMnO_4$ of a crude acid fraction to anthraquinone; some (?) 4-*hydroxy*-1 : 4-*diphenyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphtholactone*, m.p. 155·5—156°, derived from (**III**), is also formed. PhMe, (**II**), and $AlCl_3$ give 10% of 6-*methyl*-1-*naphthoic acid*, m.p. 176·5—177° [*anilide*, m.p. 167—168°; identified by (*a*) decarboxylation and subsequent dehydrogenation to 2-$C_{10}H_7Me$ and (*b*) oxidation by $K_3Fe(CN)_6$ to 1 : 6-$C_{10}H_6(CO_2H)_2$], and a little 1 : 4-*di*-p-*tolyl*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthoic acid*. Me furoate, PhMe, and $AlCl_3$ give 6 : 1-$C_{10}H_6Me{\cdot}CO_2Me$ (8%; 18% formed in CS_2), b.p. 110—114°/2 mm., and a little 2 : 7-dimethylanthracene. PhOMe, (**II**), and $AlCl_3$ give 6-*methoxy*-1-*naphthoic acid* (12%), m.p. 180—180·5°, and 1 : 4-*di*-p-*anisyl*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthoic acid*. PhCl gives similarly 6-*chloro*-1-*naphthoic acid* (18%), m.p. 188—189°, which with Cu chromite in quinoline at 225° gives 2-$C_{10}H_7Cl$. R. S. C.

1-Alkyl 2-dialkylaminoalkyl 3-aminophthalates as local anæsthetics. F. F. Blicke and C. Otsuki (*J. Amer. Chem. Soc.*, 1941, **63**, 1945—1947).—3 : 1 : 2-$NO_2{\cdot}C_6H_3(CO_2Et){\cdot}CO_2H$ and $NEt_2{\cdot}[CH_2]_2{\cdot}Cl$ in boiling $Pr^{\beta}OH$ give 1-*Et* 2-β-*diethylaminoethyl* 3-*nitrophthalate hydrochloride* (**I**) (method *A*), m.p. 126—128°. 3 : 1 : 2-$NO_2{\cdot}C_6H_3(CO)_2O$ (**II**) and $NEt_2{\cdot}[CH_2]_2{\cdot}OH$ in boiling C_6H_6 give 2-β-*diethylaminoethyl* 1-*H* 3-*nitrophthalate*, m.p. 167—168°. $SOCl_2$ then gives the acid chloride hydrochloride which in EtOH gives (**I**) (method *B*). $OH{\cdot}[CH_2]_2{\cdot}Br$ and (**II**) in C_6H_6 at 100° give 2-β-*bromoethyl* 1-*H* 3-*nitrophthalate*, m.p. 172—175°, which with $SOCl_2$ and then EtOH gives 1 : 3 : 2-$CO_2Et{\cdot}C_6H_3(NO_2){\cdot}CO_2{\cdot}[CH_2]_2{\cdot}Br$, converted by $NHEt_2$ in PhMe etc. into (**I**). Method (*A*) gives also 1-*Me*, m.p. 139—140°, and 1-*Pr*α 2-β-*diethylaminoethyl* 3-*nitrophthalate hydrochloride*, m.p. 93—95°, and 1-*Pr*α 2-γ-*dimethylamino*-ββ-*dimethyl*-n-*propyl* 3-*nitrophthalate hydrobromide*, m.p. 164—166°. Method *B* gives also 1-Pr^{β} (*hydrobromide*, m.p. 110—111°), 1-Bu^{α} (*hydrobromide*, m.p. 73—75°), 1-Bu^{β} (*methiodide*, m.p. 155—156°), 1-*sec.*-Bu (*hydrobromide*, m.p. 86—88°), 1-*n*-amyl (*hydrobromide*, m.p. 91—93°), and 1-*n*-hexyl (*methiodide*, m.p. 50—53°) 2-β-diethylaminoethyl 3-nitrophthalate. $SnCl_2$–HCl–AcOH reduces these products to 1-Me (*hydrochloride*, m.p. 114—115°), 1-Et (*hydrobromide*, m.p. 112—113°), 1-Pr^{α} (*hydrobromide*, m.p. 107—108°), 1-Pr^{β} (*citrate*, m.p. 86—89°), 1-Bu^{α} (*hydrobromide*, m.p. 91—92°), 1-Bu^{β} (*hydrobromide*, m.p. 110—112°), 1-*sec.*-Bu (*citrate*, m.p. 92—95°), 1-*n*-amyl (*citrate*, m.p. 81—83°), and 1-*n*-hexyl (*citrate*, m.p. 79—81°) 2-β-diethylaminoethyl and 1-Pr^{α} 2-γ-dimethylamino-ββ-dimethyl-*n*-propyl 3-aminophthalate (*citrate*, m.p. 145—146°). $NMe_2{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$ (hydrobromide, m.p. 157—159°) and $SOCl_2$ in C_6H_6 etc. give γ-*dimethylamino*-ββ-*dimethyl*-n-*propyl chloride hydrobromide*, m.p. 157—158°. Many of the products are strong local anæsthetics. R. S. C.

3-Hydroxy-*o*-phthalic acid. Y. Miyashita (*J. Pharm. Soc. Japan*, 1940, **60**, 199—200).—3 : 1 : 2-$OH{\cdot}C_6H_3(CO_2H)_2$ (prep.: Wegler, A., 1937, II, 213) [anhydride, new m.p. 199—201°; Me ether, m.p. 177—179° (lit. 172—174°)] has m.p. 166—167° (lit. 145—148° to 161—163°). A. T. P.

Steroids and sex hormones. LXIX. Relationships of $\Delta^{5:6-20:22}$-3 : 21-dihydroxynorcholadienolactone to uzarigenin. L. Ruzicka, P. A. Plattner, and A. Fürst (*Helv. Chim. Acta*, 1941, **24**, 716—724).—$\Delta^{5:6-20:22}$-21-Hydroxy-3-acetoxynorcholadienolactone (**I**), m.p. 174°, has been isolated from the products (A., 1941, II, 226) of the interaction of $\Delta^{5:6}$-3 : 21-diacetoxypregnen-20-one with $CH_2Br{\cdot}CO_2Et$; it is hydrolysed by 2N-HCl in dioxan at 100° to the corresponding lactone (**II**), m.p. 262—263°. (**I**) is hydrogenated (Raney Ni in EtOH and room temp.) to $\Delta^{5:6}$-21-*hydroxy*-3-*acetoxynorcholenolactone*, m.p. 188—190°, $[\alpha]_D$ −52·8° in $CHCl_3$, which gives a negative Legal test. Hydrogenation (PtO_2 in AcOH) of (**I**) affords a product from which 21-hydroxy-3-acetoxynor*allo*cholanolactone (**III**), m.p. 203—204°, $[\alpha]_D$ +15° in $CHCl_3$, is isolated. Hydrogenation and subsequent acetylation of (**II**) affords (**III**), $[\alpha]_D$ +19·7° in $CHCl_3$, and an isomeride, m.p. 243°, $[\alpha]_D$ +5·9° in $CHCl_3$. The identity of these products with those from α-anhydrouzarigenin (**IV**) appears highly probable. The *p*-nitrobenzoate, m.p. 247—248°, of (**II**) appears identical with that of (**IV**). M.p. are corr. H. W.

Bodroux–Tschitschibabin and Bouveault aldehyde syntheses. L. I. Smith and M. Bayliss (*J. Org. Chem.*, 1941, **6**, 437—442).—The max. yield of PhCHO from $CH(OEt)_3$ and MgPhHal (~90%) is secured when the reaction mixture is set aside for 15 hr. after mixing the reagents, the Et_2O is removed and the residue heated for ⩾15 min at 100° (bath), and mol. proportions of the reagents are used. With *o*-, *m*-, and *p*-C_6H_4MeBr the yields of $C_6H_4Me{\cdot}CHO$ are 51·7, 56·2, and 50·4%, respectively. The yields of PhCHO from NPhMe·CHO (**I**) and MgPhBr (**II**) are 59, 11, 67, and 67%, respectively, when the reaction is conducted in Et_2O alone, in PhMe after removal of Et_2O, by adding excess of (**II**) to (**I**) in Et_2O, or by the inverse process. With (**I**) and the Grignard compound from *o*-, *m*-, and *p*-C_6H_4MeBr, bromoquinol Me_2 ether, and 2 : 4 : 6 : 1-$C_6H_2Me_3Br$ the yields are 50, 33, 37, 20, and 18·8%, respectively. The use of $CH(OEt)_3$ is preferable to that of (**I**). H. W.

Relation between structure and odour of derivatives 2 : 2 : 4-trimethyl-Δ^3-tetrahydrobenzaldehyde. O. N. Jitkov and M. T. Bogert (*J. Amer. Chem. Soc.*, 1941, **63**, 1979—1984).—Odours are given in parentheses below. $CMe_2{:}CH{\cdot}COMe$ and MgMeI in Et_2O at <5° give a crude carbinol, dehydrated by distillation with a trace of **I** to $CMe_2{:}CH{\cdot}CMe{:}CH_2$ (**I**) (58%), b.p. 94—96°/771 mm. [$(CH{\cdot}CO)_2O$ adduct, m.p. 49—50°], which with acraldehyde at 145—150° gives 75—85% of 2 : 2 : 4-trimethyl-Δ^3-tetrahydrobenzaldehyde (**II**), b.p. 80°/12 mm. [semicarbazone, m.p. 200—201° (lit. 197—198°); 2 : 4-*dinitrophenylhydrazone*, m.p. 164—165°; *Et*$_2$ *acetal*, b.p. 126—128°/22 mm. (pine-sap), obtained by conc. HCl–EtOH at room temp.]. Ag_2O oxidises (**II**) to the acid, m.p. 86—87° (lit., b.p. 135—140°/12 mm.), dehydrogenated by Se at 270—290° to 2 : 4 : 1-$C_6H_3Me_2{\cdot}CO_2H$. Heating (**II**) with $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ with removal of $COMe_2$ gives 2 : 2 : 4-*trimethyl*-Δ^3-*tetrahydrobenzyl alcohol* (**III**) (70%), b.p. 113—113·5°/13 mm. (eucalyptus oil) [3 : 5-*dinitrobenzoate*, m.p.

63—64°; *acetate*, b.p. 115—116°/13 mm. (geranium), obtained (66%) by AcCl–C_5H_5N, first at 0° and then at room temp.]. (**III**) is not obtained from (**I**) and CH_2:CH·CH_2·OH at 200°, which gives a substance, b.p. 89—97°/10 mm. (camphor). MgMeI and (**II**) in Et_2O at 0—5° give 75% of α-2 : 2 : 4-*trimethyl*-Δ³-cyclo*hexenylethyl alcohol*, b.p. 105—107°/15 mm. (fresh mint) (*phenylurethane*, m.p. 105—105·5°). MgEtBr gives similarly α-2 : 2 : 4-*trimethyl*-Δ³-cyclo*hexenylpropyl alcohol* (70%), b.p. 118—119°/15 mm. (sweet grass) (*phenylurethane*, m.p. 109—110°). $Na_2Cr_2O_7$–H_2SO_4 oxidises the two last-mentioned alcohols to 2 : 2 : 4-*trimethyl*-Δ³-cyclo*hexenyl Me* (76%), b.p. 99—100°/13 mm. (fresh mint) (2 : 4-*dinitrophenylhydrazone*, m.p. 146—147°), and *Et ketone* (70%), b.p. 118—118·5°/18 mm. (fresh mint and fruit) (2 : 4-*dinitrophenylhydrazone*, m.p. 138—139°). $CH_2Br·CO_2Et$, Zn, and (**II**) in C_6H_6 give *Et β-hydroxy-β*-2 : 2 : 4-*trimethyl*-Δ³-cyclo*hexenylpropionate* (70%), b.p. 120—121·5°/2 mm., hydrolysed by KOH–MeOH to the *acid*, m.p. 133—134°, b.p. 150—153°/1·5 mm., the Ba salt of which on pyrolysis gives *di-β-hydroxy-β*-2 : 2 : 4-*trimethyl*-Δ³-cyclo*hexenylethyl ketone*. $COMe_2$, (**II**), and EtOH–NaOEt (temp. rises to 47°) give *β*-2 : 2 : 4-*trimethyl*-Δ³-cyclo*hexenylvinyl Me ketone* (**IV**) (66%), b.p. 254—256°/760 mm., 135°/12 mm. (spicy cedarwood; when dil., violet) (*semicarbazone*, m.p. 183—184°; 2 : 4-*dinitrophenylhydrazone*, m.p. 143—144°), which with P_2O_5 (I is unsatisfactory) at 90° (bath)/reduced pressure yields 1 : 1 : 3-*trimethyl*-1 : 4 : 6 : 9-*tetrahydronaphthalene* (47%), b.p. 132—134°/12 mm. This gives no adduct with (CH·CO)$_2$O in PhMe at 100° and, when heated with S, gives 1 : 3-$C_{10}H_6Me_2$ [picrate, m.p. 116—117° (lit. 118°); *styphnate*, m.p. 132—133°]. CH_2:CH·CH_2·MgBr and (**IV**) in boiling Et_2O give α-2 : 2 : 4-*trimethyl*-Δ³-cyclo*hexenyl-γ-methyl*-Δ$^{\alpha\epsilon}$-*hexadien-γ-ol* (65%), b.p. 104—105°/2 mm., unstable at the b.p./9 mm. (rhubarb), dehydrated by $SOCl_2$–C_5H_5N in Et_2O at −5° to products, which after digestion with Na at 125° yield α-2 : 2 : 4-*trimethyl*-Δ³-cyclo*hexenyl-γ-methyl*-Δ$^{\alpha\gamma\epsilon}$-*hexatriene* (54%), b.p. 103—104°/3 mm. (lemon-verbena; sensitive to light; polymerises when kept; turbid violet $SbCl_3$ colour). MeCHO and (**II**) in presence of piperidine acetate give *δ-hydroxy-δ*-2 : 2 : 4-*trimethyl*-Δ³-cyclo*hexenyl*-Δ$^{\alpha}$-*pentenoaldehyde*, b.p. 90—94°/6 mm., whence only the semicarbazone of (**II**) is obtained. Relations between structure and odour are discussed. In the ionone series an odour of violets requires a *cyclo*hexene nucleus carrying ≮3 Me, of which two must be adjacent to the side-chain as *gem.*-Me_2 or as single Me on each side; the position of the ethylenic linking affects the quality, but not the type, of odour, but introduction of a second such linking changes the type. M.p. and b.p. are corr. R. S. C.

Condensation of aromatic compounds with acids. I. Condensations with hydrocarbons, phenol, and phenetole. I. Tzukervanik and I. Terentieva (*J. Gen. Chem. Russ.*, 1940, **10**, 1405—1407).—The reactions PhR + R′CO_2H → *o*- and *p*-COR′·C_6H_4R (R = Me, OEt, OH; R′ = Bu$^{\beta}$, Pr$^{\alpha}$) are effected in presence of $AlCl_3$. R. T.

Synthesis of ketone derivatives of diphenyl by the Friedel–Crafts reaction. L. M. Long and H. R. Henze (*J. Amer. Chem. Soc.*, 1941, **63**, 1939—1940).—Ph_2 (1), RCOCl (1·1), and $AlCl_3$ (1·1 mol.) in CS_2 give 4-acetyl-, m.p. 121°, -propionyl-, m.p. 89°, -*n*-, m.p. 94°, and -*iso*-butyryl-, m.p. 62°, -n-*valeryl*-, m.p. 76—78°, -*iso*valeryl-, m.p. 74—76·5°, -n-, m.p. 96·5°, and -iso-*hexoyl*-, m.p. 71—72·5°, -α-*methyl*-n-*valeryl*-, m.p. 64°, -α-*ethyl*-n-*butyryl*-, m.p. 77—79°, -benzoyl-, m.p. 106°, and -n-*heptoyl-diphenyl*, m.p. 85·5—86·5°. Ph_2 (1), RCOCl (3), and $AlCl_3$ (3 mols.) in CS_2 give also much 4 : 4′-di-acetyl-, m.p. 191°, -propionyl-, m.p. 168°, -n-, m.p. 174·2°, and -iso-*butyryl*-, m.p. 103°, -n-, m.p. 162—163°, and -iso-*valeryl*-, m.p. 113°, -n-, m.p. 164·5°, and -iso-*hexoyl*-, m.p. 138—140°, -benzoyl-, m.p. 218°, and -n-*heptoyl-diphenyl*, m.p. 157·1°. The (CHMePr$^{\alpha}$·CO)$_2$ and (CHEt$_2$·CO)$_2$ compounds could not be obtained. M.p. are corr. R. S. C.

Molecular rearrangements involving optically active radicals. IX. Wolff rearrangement of optically active diazo-ketones. J. F. Lane and E. S. Wallis (*J. Org. Chem.*, 1941, **6**, 443—451).—6-Nitro-2-methyldiphenyl-2′-carboxylic acid is converted into the chloride, m.p. 85°, and thence by CH_2N_2 in dry Et_2O at −10° into ω-diazo-*o*-6′-nitro-2′-methylphenylacetophenone (**I**), identified by conversion (glacial AcOH at 80°) into *ω-acetoxy*-o-6′-*nitro*-2′-*methylphenylacetophenone*, m.p. 125°. (**I**) is rearranged by boiling NH_2Ph to o-(6′-*nitro*-2′-*methylphenyl*)-*phenylacetanilide* (**II**), m.p. 137°, and by Ag_2O–$Na_2S_2O_3$ in aq. dioxan at 65—70° to the -phenylacetic acid, an oil, identified by transformation into (**II**). Similarly, *d*-6-nitro-2-methyldiphenyl-2′-carboxylic acid, $[\alpha]_D^{20}$ +70·0° in MeOH, is converted into the non-cryst. *d*-ω-diazo-ketone (**III**), $[\alpha]_D^{20}$ +115° in $CHCl_3$, and an impure *l*-form, $[\alpha]_D^{20}$ −46·1° in $CHCl_3$, is derived from a non-homogeneous *l*-acid, $[\alpha]_D^{20}$ −28·0° in MeOH. Rearrangements of (**III**) in boiling NH_2Ph and in aq. dioxan lead to d-(**II**), m.p. 124°, $[\alpha]_{5583}^{20}$ +369°, $[\alpha]_{5893}^{20}$ +481°, $[\alpha]_{5463}^{20}$ +624°, $[\alpha]_{2801}^{20}$ +875° in $CHCl_3$, and the corresponding non-cryst. acid, $[\alpha]_D^{20}$ +53·0° in $CHCl_3$; no racemisation is observed in either case. *d*-α-Phenyl-α-methylhexoic acid is converted (boiling $SOCl_2$) into the chloride and thence into *d*-α-diazo-γ-phenyl-γ-methylheptan-β-one (**IV**), $[\alpha]_D^{20}$ +65·0° in C_6H_6; an impure *l*-isomeride, $[\alpha]_D^{20}$ −29·4° in C_6H_6, is recorded. Rearrangements of (**IV**) lead to *β-phenyl-β-methyl-heptanilide* (**V**), m.p. 76°, $[\alpha]_{5563}^{20}$ −47·2°, $[\alpha]_{5893}^{20}$ −59·5°, $[\alpha]_{5463}^{20}$ −72·2°, $[\alpha]_{4801}^{20}$ −96·0° in C_6H_6, and -heptoic acid, identified by conversion into (**V**); no evidence of racemisation is obtained. *d*-$CH_2Ph·CHMe·CO·CHN_2$ (**VI**), α_D^{20} +134° (*l* = 1) (A., 1940, II, 279), is converted by boiling NH_2Ph into r-*γ-phenyl-β-methylbutyranilide*, m.p. 102°, inactivation being complete. Racemisation of optically active diazo-ketones during the Wolff rearrangement is by no means a general phenomenon. The partial or complete racemisation of the products resulting from (**VI**) is attributed to the presence of enolisable H at the asymmetric centre. That enolisation and racemisation occur in the Wolff rearrangement and not in the Hofmann rearrangement where the $CH_2Ph·CHMe·$ group is involved is attributed to the presence of the metallic catalyst in the former reaction. H. W.

Atom displacement during the bromination of *o*-nitrodiphenylmethane. P. Ruggli and B. Hegedus (*Helv. Chim. Acta*, 1941, **24**, 703—716).—*o*-$NO_2·C_6H_4·CH_2Ph$ (**I**) does not condense with PhCHO or $COPh_2$ in presence of KOH or piperidine and does not react with CPh_2Cl_2. Like *o*-$NH_2·C_6H_4·CO_2Ph$ and *o*-$NHAc·C_6H_4·CO_2Ph$, *o*-$NO_2·C_6H_4·COPh$ is indifferent towards PCl_5. (**I**) does not react with Br in boiling CCl_4 but in boiling $C_2H_2Cl_4$ it gives 85% of 3 : 5-*dibromo*-2-*aminobenzophenone* (**II**), m.p. 98°, obtained in poorer yield by bromination of (**I**) without solvent at 140—145°. (**II**) is indifferent towards NaI or C_5H_5N, does not absorb H_2 in presence of Raney Ni, and is converted by molten KOH into BzOH and 2 : 4 : 1-$C_6H_3Br_2·NH_2$. Catalytic dehalogenation (Pd–$CaCO_3$ in alkaline MeOH) of (**II**) leads to *o*-$NH_2·C_6H_4·COPh$, from which (**II**) is readily obtained by the action of Br in cold $CHCl_3$. Acetylation of (**II**) with Ac_2O proceeds smoothly only in the presence of a little H_2SO_4 and then, according to conditions, gives a normal, freely sol. *Ac* derivative (**III**), m.p. 156°, and a Ac_2 derivative (**IV**), m.p. 134°, with small amounts of an imperfectly explained *substance* (**V**), m.p. 230° (decomp.), isomeric with (**III**) and provisionally regarded as an *iso*-Ac substance. Under mild conditions (aq. Na_2CO_3) (**IV**) is hydrolysed to (**III**), which is converted into (**II**) by 40% H_2SO_4–EtOH. Boiling, very dil. KOH partly hydrolyses (**III**) but mainly transforms it into 6 : 8-*dibromo*-4-*phenylcarbostyril*, m.p. 210—211°, debrominated to 4-phenylcarbostyril, m.p. 259°. (**V**) is distinguished from (**III**) by its sparing solubility and its colour reactions. Short treatment with boiling dil. H_2SO_4 converts (**V**) into (**II**) but debromination leads to an unidentified *compound*, $C_{15}H_{11}ON$, m.p. 161°. (**II**) is reduced by Na–Hg in aq. EtOH at room temp. to 5-*bromo*-2-*aminobenzhydrol* (**VI**), m.p. 113° (Br is considered to be removed from $C_{(3)}$ since, under similar treatment, 2 : 4 : 1-$C_6H_3Br_2·NH_2$ is converted into *p*-$C_6H_4Br·NH_2$). (**VI**) is debrominated to *o*-aminobenzhydrol (**VII**), m.p. 118—119°. Na and 95% EtOH at 50—60° reduce (**II**) to 3 : 5-*dibromo*-2-*aminobenzhydrol*, m.p. 152°, debrominated to (**VII**). Reduction of (**II**) by Zn dust in boiling AcOH appears complex, the only product isolated being 3 : 5-*dibromo*-2-*acetamidodiphenylmethane*, m.p. 194°; this is debrominated to *o*-$NHAc·C_6H_4·CH_2Ph$, m.p. 127—130°, from which it is readily prepared by bromination in AcOH containing NaOAc. (**II**) and MgEtI yield α-*phenyl*-α-3 : 5-*dibromo*-2-*aminophenylpropyl alcohol*, m.p. 109° (debrominated to *o*-$NH_2·C_6H_4·CPhEt·OH$, m.p. 102°). With MgPhBr (**II**) gives 3 : 5-*dibromo*-2-*aminotriphenylcarbinol*, m.p. 116°, debrominated to *o*-$NH_2·C_6H_4·CPh_2·OH$, m.p. 122°. (**II**) is oxidised by CrO_3 in boiling AcOH to 4 : 6 : 4′ : 6′-*tetrabromo*-2 : 2′-*dibenzoylazobenzene*, m.p. 242°. Under similar conditions *o*-$NH_2·C_6H_4·COPh$ gives 2 : 2′-dibenzoylazobenzene, m.p. 199—200°. Gradual addition of MgPhBr in Et_2O to

well-cooled *o*-NO_2·C_6H_4·CHO in Et_2O gives a non-cryst. product which cannot be distilled in a vac.; it does not react with Ac_2O, PCl_3, PBr_3, HCl in C_6H_6, or PhNCO but is oxidised to *o*-NO_2·C_6H_4·COPh with a small proportion of acidic products. H. W.

Aromatic αγ-diketones.—See B., 1941, II, 298.

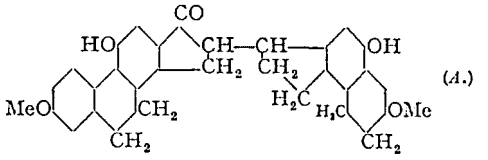
Synthesis of substances related to the sterols. XXIX. (Sir) R. Robinson and S. N. Slater (*J.C.S.*, 1941, 376—385; cf. A., 1940, II, 16).—The oxime of 3-keto-7-methoxy-1 : 2 : 3 : 9 : 10 : 11-hexahydro-1 : 2-*cyclo*pentenophenanthrene-*A* (**I**) (A., 1938, II, 145) and Na–BuOH afford 3-amino-7-methoxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydro-1 : 2-*cyclo*pentenophenanthrene [isomeric *hydrochlorides*, m.p. 302° and 272° (viscous), 278° (mobile) (sinters at 258°)]. 3-Keto-1 : 2 : 3 : 9 : 10 : 11-hexahydro-1 : 2-*cyclo*pentenophenanthrene (modified prep.) and $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ yield 3-*hydroxy*-1 : 2 : 3 : 9 : 10 : 11-*hexahydro*-, m.p. 131—132° (softens at 128°), dehydrated ($KHSO_4$ at 160—180° under reduced pressure) to 1 : 9 : 10 : 11-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 79°, which is converted by SeO_2–EtOH at 100° (bath) into (probably) 9 : 10-*dihydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 61—62°, and some ketonic substance. Pondorff reduction of (**I**) affords 3-*hydroxy*-7-*methoxy*-1 : 2 : 3 : 9 : 10 : 11-*hexahydro*- (**II**), m.p. 157—161°, converted by $KHSO_4$ (dehydrates and dehydrogenates) into (probably) 7-*methoxy*-9 : 10-*dihydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 101—102°. The Me xanthate of (**II**) at 180° under reduced pressure yields a little 7-*methoxy*-1 : 9 : 10 : 11-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 82—85°. *cyclo*Hexanone, acetyl*cyclo*pentene, and C_5H_5N–KOPr$^{\beta}$–Pr$^{\beta}$OH–Et_2O at 100° (bath) afford 3-*keto*-$\Delta^{4:10}$-*octahydro*-, isomerides, b.p. 110—115°/0·28 mm. (*A*) and 125—140°/0·28 mm. (*dinitrophenylhydrazone*, m.p. 164—165°), and reduction (Na–EtOH) of *A* gives 3-hydroxydecahydro-, b.p. 110—130°/high vac., and thence (method: Oppenauer, A., 1937, II, 250) (?) 3-*keto*-*decahydro*-1 : 2-cyclo*pentenonaphthalene*, b.p. 120—130°/0·74 mm. The latter and MgMeI afford 3-*hydroxy*-3-*methyldecahydro*-1 : 2-cyclo*pentenonaphthalene*, b.p. 108—128°/0·22 mm., dehydrated by $KHSO_4$ at 180—190° to (probably) 3-*methyl*-$\Delta^{2 \text{ or } 3}$-*octahydro*-1 : 2-cyclo*pentenonaphthalene*, b.p. 90—93°/0·17 mm. 2-$C_{10}H_7$·MgBr and Et lævulate give γ-*hydroxy*-γ-2-*naphthylvalerolactone* (**III**), m.p. 77°, some (2-$C_{10}H_7)_2$, and (probably) (**IV**) (below). (**III**) is also obtained, together with γ-2-*naphthyl*-Δ^{β}-*pentenoic acid* (**IV**), m.p. 141—142° [hydrated (dil. H_2SO_4 at 100°) to (**III**)], from Et or Me β-2-naphthoylpropionate and MgMeI, best in boiling C_6H_6–Et_2O. Et β-1-naphthoylpropionate and MgMeI yield γ-1-naphthyl-Δ^{β}-pentenoic acid. 6 : 2-OMe·$C_{10}H_6$·MgBr (**V**) (+MgMeI) and Et lævulate in C_6H_6–Et_2O afford γ-6-methoxy-2-naphthyl-Δ^{β}-pentenoic acid, new m.p. 177°, but cyclisation was not effected. (**V**) and Et *cyclo*pentanone-3-carboxylate afford the *lactone*, m.p. 97—98°, of 3-hydroxy-3-(6′-methoxy-2′-naphthyl)*cyclo*pentane-1-carboxylic acid. 3′-Keto-4-methoxy-1 : 2-*cyclo*pentenophenanthrene (**VI**) and MgEtBr yield 4-*methoxy*-3′-*ethyl*-$\Delta^{3'}$-1 : 2-cyclo*pentenophenanthrene*, m.p. 105° (previous softening). (**VI**), CH_2Br·CO_2Et, and Zn wool in C_6H_6–PhMe give *Et* 4-*methoxy*-1 : 2-cyclo*pentenophenanthrylidene*-3′-*acetate* (**VII**), m.p. 144°, hydrogenated (Pd–C; EtOH) to (after hydrolysis) 4-*methoxy*-1 : 2-cyclo*pentenophenanthrene*-3′-*acetic acid*, m.p. 169°. (**VII**) is reduced (Raney Ni at 200–220°/~65 atm.) with loss of OMe to 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-1 : 2-cyclo*pentenophenanthrene*-3′-*acetic acid*, isomerides, m.p. 196° (mainly) and 148°. *Et* 4 : 7-*dimethoxy*-1 : 2-cyclo*pentenophenanthrylidene*-3′-*acetate* (**VIII**), m.p. 192° [prepared similarly to (**VII**)], is hydrogenated (Pd–C or Raney Ni) to *Et* 4 : 7-*dimethoxy*-1 : 2-cyclo*pentenophenanthrene*-3′-*acetate* (**IX**), m.p. 106—107° (free *acid*, m.p. 197°), or (Raney Ni–EtOH; ~200°/65 atm. for 16 hr. and repeat) to *Et* 7-*methoxy*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydro*-1 : 2-cyclo*pentenophenanthrene*-3′-*acetate*, b.p. 218—222°/0·5 mm. Hydrogenation of (**IX**) (Raney Ni–EtOH; 200—220°/65 atm. for 8 hr.) causes elimination of 2 OMe to form a *substance* (**X**), $C_{19}H_{24}O_2$, m.p. 190—193°, and a product, m.p. ~178—180°, probably a mixture of (**X**) and $C_{20}H_{26}O_3$. A. T. P.

Synthesis of substances related to the sterols. XXX. (Sir) R. Robinson and F. Weygand. **XXXI.** J. G. Cook and (Sir) R. Robinson. **XXXII.** (Sir) R. Robinson and J. Willenz. **XXXIII. Hydrogenation of *cyclo*pentenonaphthalene derivatives.** L. C. Bateman and (Sir) R. Robinson (*J.C.S.*, 1941, 386—391, 391—393, 393—397, 398—404).—XXX. 1 : 2-$C_{10}H_6$Me·OH (prep: discussed and modified) is reduced [H_2 (3—4 atm.), PtO_2; AcOH] to 1-*methyldecahydro*-2-*naphthol*, b.p. 121—123°/16 mm. (probably a mixture of stereoisomerdes which are derivatives of *cis*-decahydronaphthalene), which is oxidised ($K_2Cr_2O_7$–aq. H_2SO_4 at 65°) to 2-keto-1-methyl-*cis*-decahydronaphthalene, b.p. 117—120°/15 mm. (purified through the *semicarbazone*, m.p. 185—191°; 2 : 4-*dinitrophenylhydrazone*, m.p. 144—146°), converted by $NaNH_2$–Et_2O at 20° (N_2), followed by COMe·$[CH_2]_2$·NMeEt_2I in EtOH (method; A., 1937, II, 196), into 2-keto-12-methyl-$\Delta^{1:11}$-dodecahydrophenanthrene (**I**), b.p. 126—190°/16 mm. [*semicarbazone*, m.p. 225—230° (decomp.)], which with Se at 340° affords phenanthrene and 2-hydroxyphenanthrene. (**I**) may be a mixture of two stereoisomerides; if it is a pure substance there is no sound indication of the disposition of the Me group relative to ring c. 2 : 6-OH·$C_{10}H_6$·OMe, 40% aq. CH_2O, and N-NaOH at 100° (bath) afford 1 : 1′-*methylenebis*-2-*hydroxy*-6-*methoxynaphthalene*, m.p. 202°. 2 : 6-$C_{10}H_6(OH)_2$ is reduced (as for 1 : 2-$C_{10}H_6$Me·OH) to *cis*-decahydro-β-naphthol. 2 : 6-$C_{10}H_6(OR)_2$ (R = Ac, Me) give deoxygenated products on catalytic reduction. 2 : 6-$C_{10}H_6(OMe)_2$, *iso*-C_5H_{11}·OH, and Na (reflux) give (?) 2 : 6-*dimethoxy*-3 : 4-*dihydronaphthalene*, m.p. 83—84°. 1 : 2-$C_{10}H_6$Me·OMe and AcCl (Friedel–Crafts) yield 6-*methoxy*-5-*methyl*-2-*acetonaphthone*, m.p. 97—98° [2 : 4-dinitrophenylhydrazone, m.p. 282—283°; *oxime*, m.p. 171°; HI (*d* 1·7)–AcOH afford the 6-*OH*-compound, m.p. 164°], converted by aq. NaOCl–NaOH into the corresponding 2-*naphthoic acid*, m.p. 266—267°. Demethylation then yields 6-*hydroxy*-5-*methyl*-2-*naphthoic acid*, m.p. 247—249°, which is reduced (H_2, PtO_2; AcOH) to 5-*methyldecahydro*-2-*naphthoic acid*, m.p. 127—128°. 1 : 5-$C_{10}H_6(OH)_2$ and CH_2Ac·CO_2Et–EtOH–HCl at 0—30° afford 6′-*hydroxy*-4-*methyl*-7 : 8-*benzcoumarin*, m.p. 299—302° (decomp.) (p-*nitrobenzoate*, m.p. 262°), converted by CH_2Ac·CO_2Et–H_2SO_4 at 110—120° (bath) into 4 : 4′-*dimethyl*-7 : 8 : 8′ : 7′-*coumarinocoumarin*, sublimes at 290—300°/0·05 mm., m.p. >360°, which has a mol. shape and disposition of O atoms that have some resemblance to the corresponding features of the sex hormones.

XXXI. Attempts to obtain compounds closely allied to testosterone are described. 4-Methoxy*cyclo*hexanone, $NHEt_2$, HCl, and aq. EtOH–paraformaldehyde afford impure 4-methoxy-2-diethylaminomethyl*cyclo*hexanone (distillation gives a N-free *compound*, b.p. 175°/20 mm.), thence its methiodide, which condenses with CHNaAc·CO_2Et–EtOH to a product, from which monocyclic diketone is removed by NaOEt–Et_2O or 50% H_2SO_4 at 50°, to give 2-*keto*-6-*methoxy*-$\Delta^{1:9}$-*octahydronaphthalene* (**II**), b.p. 170—175°/20 mm. (could not be converted into an oxide). MgMeI and (**II**) probably afford a 6-*methoxy*-2-*methylhexahydronaphthalene*, b.p. 125—130°/15 mm. (**II**) is reduced (Wolff or Clemmensen) to 6-*methoxy*-$\Delta^{1:9}$-*octahydronaphthalene*, b.p. 110°/15 mm. (the chlorohydrin could not be prepared), or catalytically (Pd–$SrCO_3$–MeOH) to 2-*keto*-6-*methoxydecahydronaphthalene*, b.p. 150°/15 mm. Et sodio-β-ketovalerate (**III**) in place of CHNaAc·CO_2Et (above) affords 2-keto-6-methoxy-1-methyl-$\Delta^{1:9}$-octahydronaphthalene, b.p. 145°/15 mm., hydrogenated to 2-*keto*-6-*methoxy*-1-*methyldecahydronaphthalene*, b.p. 140°/10 mm., which is converted by COMe·$[CH_2]_2$·NMeEt_2I and $NaNH_2$ in Et_2O–EtOH (N_2) into 2-*keto*-7-*methoxy*-12-*methyl*-$\Delta^{1:11}$-*dodecahydrophenanthrene*, b.p. 170°/1 mm. Et *cyclo*hexanone-4-carboxylate (as above) affords Et 2-diethylaminomethyl*cyclo*hexanone-4-carboxylate, thence the methiodide, which with (**III**) gives Et 2-keto-1-methyl-$\Delta^{1:9}$-octahydronaphthalene-6-carboxylate, b.p. 197°/10 mm., hydrogenated (Pd–$SrCO_3$, C, MeOH) to *Et* 2-*keto*-1-*methyldecahydronaphthalene*-6-*carboxylate*, b.p. 180—190°/10 mm., converted into *Et* 2-*keto*-12-*methyl*-$\Delta^{1:11}$-*dodecahydrophenanthrene*-7-*carboxylate*, b.p. 180°/1 mm. Reduction (Pondorff) of the latter compound, interaction of the resulting product with MgEtBr, and subsequent oxidation (Oppenauer) gives a non-androgenic product (possibly 2-keto-12-methyl-7-α-hydroxy-α-ethylpropyl-$\Delta^{1:11}$-dodecahydrophenanthrene) which is a close analogue of testosterone.

XXXII. 5-*Chloro*-6-*methoxy*-2-*acetonaphthone*, m.p. 124°, b.p. 192°/1·7 mm. [2 : 4-*dinitrophenylhydrazone*, m.p. 298° (decomp.); *piperonylidene* derivative, m.p. 199—201°], is obtained from 1 : 2-$C_{10}H_6Cl$·OMe, $AlCl_3$, and AcCl–$PhNO_2$ at 0° to room temp. Hydrolysis (boiling EtOH–conc. HCl) of its *furfurylidene* derivative, m.p. 151—152°, gives γζ-*diketo*-ζ-(5-*chloro*-6-*methoxy*-2-*naphthyl*)*heptoic acid*, m.p. 193—194°, converted by 2% aq. KOH at 100° (bath) into 3-(5′-*chloro*-6′-*methoxy*-2′-*naphthyl*)-Δ^2-cyclo*pentenone*-2-*acetic acid*, m.p. 215° (decomp.) (previous sintering), and thence by boiling Ac_2O

into 8-*chloro*-3′-*keto*-4-*acetoxy*-7-*methoxy*-1 : 2-cyclo*pentenophenanthrene* (**IV**), m.p. 254—255° (decomp.) (*oxime*, darkens 280—320°, not melted at 370°). The Cl of (**IV**) could not be eliminated by reduction processes; hydrolysis (aq. EtOH–NaOH) gives the 4-*hydroxy*-7-*methoxy*- (**V**), m.p. 335° (decomp. from 300°), and thence (Me_2SO_4–aq. NaOH at 40—50°) the 4 : 7-*dimethoxy*-derivative, m.p. 247°. (**IV**) and HBr (*d* 1·5)–AcOH afford apo*chlorodihydroxyketo*cyclo*pentenophenanthrene*, $C_{17}H_{11}O_3Cl$, m.p. >380°, methylated to a *Me*$_2$ *ether*, m.p. 335° (decomp.). (**IV**) is hydrogenated (Raney Ni in AcOH under pressure) to some 8-*chloro*-4-*hydroxy*-3′-*keto*-7-*methoxy*-9 : 10-*dihydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 236—237°. It is probable that the product, m.p. 139—140°, obtained from 3′-keto-4-acetoxy-7-methoxy-1 : 2-*cyclo*pentenophenanthrene (**VI**) and regarded as a *sec.* alcohol (A., 1939, II, 511), and the acetate, m.p. 145°, are 4-*hydroxy*-3′-*keto*-7-*methoxy*-9 : 10-*dihydro*-1 : 2-cyclo*pentenophenanthrene* and its acetate, respectively. Reduction of (**VI**), using Raney Ni in AcOH at 155°/50 atm. for 25 hr., affords some of a *compound* [probably (*A*)], m.p. 313° after slight sintering.



(*A*.)

Reduction (Na, *iso*-C_5H_{11}·OH) of (**V**) gave (in one case) a phenolic, non-ketonic *product*, m.p. 292° (sinters from 270°). (**VI**) and HBr (*d* 1·5)–AcOH give apo*dihydroxyketo*cyclo*pentenophenanthrene*, m.p. >380° [Me_2 ether, m.p. 301° (decomp.)], different from the 4 : 7-dihydroxy-3′-keto-1 : 2-*cyclo*pentenophenanthrene, m.p. 338° (decomp.), described previously (*loc. cit.*).

XXXIII. γζ-Diketo-ζ-*p*-anisylheptoic acid [formation of a *mono*-2 : 4-*dinitrophenylhydrazone*, m.p. 163—165° (decomp.) and a *monosemicarbazone*, m.p. 166° (decomp.), illustrates the relative inactivation of one CO] affords 3-p-*anisyl*-Δ^2-cyclo*pentenone*-2-*acetic acid*, m.p. 133° (*hydrate*), converted by Ac_2O at 170—190° (sealed tube) or by boiling (EtCO)$_2$O into 3′-*keto*-4-*acetoxy*- (**VII**), m.p. 194° [*oxime acetate*, m.p. 196° (decomp.) (previous darkening)], or -*propionoxy*-6-*methoxy*-1 : 2-cyclo*pentenonaphthalene*, m.p. 160°, respectively. (**VII**) is converted (aq. NaOH–EtOH) into 4-*hydroxy*-3′-*keto*-6-*methoxy*-, m.p. 250—255° to a black tar after darkening at ~235°, or (Me_2SO_4–aq. KOH–EtOH) 3′-*keto*-4 : 6-*dimethoxy*-1 : 2-cyclo*pentenonaphthalene* (**VIII**), m.p. 156° [*oxime* (**IX**), m.p. 236° (decomp.)]. (**VII**) is hydrogenated (Raney Ni, EtOH; 95—100 atm. at 135—145°) to (probably) 5 : 6 : 7 : 8-*tetrahydro*-1 : 2-cyclo*pentenonaphthalene*, b.p. 120—125°/0·3 mm., its 4-*hydroxy*-6-*methoxy*-derivative, m.p. 126—127° (*p*-*nitrobenzeneazo*-derivative, m.p. 173°), and an oil, b.p. 125—145°/0·3 mm. (**IX**) is hydrogenated (Raney Ni, dioxan; 100 atm. at 100—200°) to 4 : 6-*dimethoxy*-1 : 2-cyclo*pentenonaphthalene*, m.p. 84—85° (*picrate*, m.p. 164—165°). (**VIII**)–$MgPr^{\beta}Br$–PhOMe afford a small yield of 4 : 6-*dimethoxy*-3′-*iso*-*propylidene*-1 : 2-cyclo*pentenonaphthalene*, m.p. 98—99°. (**VIII**) and $CH_2Br{\cdot}CO_2Et$ or CHBrMe·CO_2Et and Zn–C_6H_6 give the yellow 4 : 6-*dimethoxy*-3′-(*carbethoxymethylene*)-1 : 2-cyclo*penteno*- (**X**), m.p. 162—163° (corresponding acid not obtained pure), or the colourless 4 : 6-*dimethoxy*-3′-(α-*carbethoxyethyl*)-1 : 2-cyclo*pentadieno*-*naphthalene*, m.p. 95° (corresponding *acid*, m.p. 172°), respectively. Hydrogenation (Raney Ni–EtOH; 150—200°/150 atm.) of (**X**) gives a mixture, m.p. ~45—50°, of H_6-derivatives; fractional crystallisation yields 4 : 6-*dimethoxy*-3′-(*carbethoxymethyl*)-5 : 6 : 7 : 8-(or 1 : 2 : 3 : 4-)*tetrahydro*-1 : 2-cyclo*pentenonaphthalene*, m.p. 83—83·5°, and a little of the corresponding (impure) 4-*OMe*-compound, m.p. 70—74°, whilst hydrolysis (aq. KOH–MeOH) of the crude reaction product affords 4(or 6)-*methoxy*- (impure) and 4 : 6-*dimethoxy*-, m.p. 117—118°, -3′-(*carboxymethyl*)-*tetrahydro*cyclo*pentenonaphthalene*. A. T. P.

Preparation of Δ^4-pregnen-20-ol-3-one and intermediates.—See B., 1941, III, 245.

New αβ-unsaturated ketone from adrenal gland. J. J. Pfiffner and H. B. North (*J. Biol. Chem.*, 1941, **140**, 161—166).—A *ketone* (**I**), $C_{21}H_{28-30}O_4$, m.p. 261—264° (decomp.) (depending on the rate of heating), $[\alpha]_D^{33}$ +133±4° in $CHCl_3$ (*semicarbazone*, sinters ~230°; *monoacetate*, m.p. 208—210°), is isolated from the second Et_2O-sol. fraction of adrenal extract (cf. A., 1941, II, 259) by treatment with Girard's reagent *T*, fractional hydrolysis of the hydrazones, and fractional esterification with $(CH_3{\cdot}CO)_2O$ in C_5H_5N. Oxidation (CrO_3, AcOH, room temp.) of (**I**) yields a *ketone*, $C_{21}H_{26-28}O_4$, m.p. 206—208° (different from adrenosterone) [*monosemicarbazone*, m.p. 242—245° (decomp.)], the absorption spectrum of which resembles that of (**I**). (**I**) is physiologically inactive. A. Li.

Vitamin-*E*. XXVIII. Synthesis of the three dimethylethylbenzoquinones. L. I. Smith and J. W. Opie (*J. Org. Chem.*, 1941, **6**, 427—436).—3 : 5 : 1-$C_6H_3Me_2{\cdot}$OAc, b.p. 118—120°/19 mm., is converted by $AlCl_3$ at 0° and then at 100° into 2 : 4 : 6 : 1-OH·$C_6H_2Me_2{\cdot}$COMe, m.p. 57—58·5° (yield 80%), which is reduced (Clemmensen) or catalytically (Raney Ni–EtOH–H_2 at 175°/2000 lb.) to 3 : 5 : 2 : 1-$C_6H_2Me_2Et{\cdot}$OH, m.p. 79—80°. This is coupled with diazotised *p*-$SO_3H{\cdot}C_6H_4{\cdot}NH_2$ (**I**) and the product is reduced ($Na_2S_2O_4$) to 4-*amino*-3 : 5-*dimethyl*-2-*ethylphenol*, m.p. 158—159° (decomp.), oxidised by $FeCl_3$ in 30% HCl to 2 : 6-dimethyl-3-ethyl-*p*-benzoquinone, b.p. 111°/10·5 mm., which is reduced (Zn and boiling aq. AcOH) to the corresponding quinol, m.p. 158—158·5°. 1 : 2 : 3-$C_6H_3Me_2{\cdot}NO_2$ is quantitatively reduced (H_2, Raney Ni) to *o*-3-xylidine, which is transformed into *o*-3-xylenol, m.p. 65—69°, either by diazotisation followed by treatment with hot H_2O [purification difficult owing to simultaneous formation of (?) 4-methylindazole] or by conversion into 1 : 2 : 3-$C_6H_3Me_2I$, which is treated with aq. NaOH and Cu wool at 275°. The acetate, b.p. 112—113°/12·5 mm., is rearranged by $AlCl_3$ to 2 : 3 : 4 : 1-OH·$C_6H_2Me_2{\cdot}$COMe, b.p. 127—129°/10·5 mm. [*semicarbazone*, m.p. 247° (decomp.)], which is reduced [Clemmensen or catalytically (Cu chromite)] to 2 : 3 : 6 : 1-$C_6H_2Me_2Et{\cdot}$OH, m.p. 52—53°. This is converted by aid of (**I**) into 4-*amino*-2 : 3-*dimethyl*-6-*ethylphenol*, 138—139° (decomp.), which yields successively 2 : 3-*dimethyl*-6-*ethyl*-p-*benzoquinone*, b.p. 111°/9 mm., m.p. 37—38°, and -*quinol*, m.p. 160—160·5°. 2 : 5 : 1-$C_6H_3Me_2{\cdot}$OH is transformed into 4-*amino*-2 : 5-*dimethylphenol*, m.p. 241° (decomp.) after darkening at 220° and softening at 238°, oxidised to *p*-xyloquinone (**II**), m.p. 123—125°, reductively acetylated to p-*xyloquinol diacetate*, m.p. 133—134°. (**II**) is converted through the quinol into 2 : 5 : 1 : 4-$C_6H_2Me_2(OMe)_2$, transformed by warm Br in CCl_4 into 2-*bromo*-3 : 6-*dimethoxy*-p-*xylene* (**III**), m.p. 59—60°, and by $Zn(CN)_2$ and HCl in C_6H_6 followed by $AlCl_3$ and HCl into 3 : 6-*dimethoxy*-2 : 5-*dimethylbenzaldehyde* (**IV**), m.p. 55—56° (*semicarbazone*, m.p. 216—217°). (**IV**) is converted by MgMeBr into α-3 : 6-*dimethoxy*-2 : 5-*dimethylphenylethyl alcohol* (**V**), b.p. 154—156°/8 mm., also obtained by the successive actions of Mg + EtBr and MeCHO on (**III**). (**V**) is unchanged by H_2 at 175°/2650 lb. in presence of Raney Ni but is converted by distillation under 8 mm. with a little H_2SO_4 into 3 : 6-dimethoxy-2 : 5-dimethylstyrene (**VI**), b.p. 125—129°/8 mm. Impure 2 : 5-dimethoxy-3-ethyl-*p*-xylene, b.p. 119—120°/8 mm., is obtained from (**III**) by the action of Mg and EtBr in Et_2O followed by Et_2SO_4 or from (**VI**) by catalytic reduction (Raney Ni; not Cu chromite). It is hydrolysed (HBr in AcOH) and then oxidised ($FeCl_3$) to 2 : 5-*dimethyl*-6-*ethyl*-p-*benzoquinone*, an oil, reduced to the *quinol*, m.p. 161—163°. H. W.

Sensitive colour reaction for 2-methyl-1 : 4-naphthaquinone and related compounds. A. Novelli (*Science*, 1941, **93**, 358).—The sensitivity and stability of the colour reaction described by Dam *et al.* (A., 1939, III, 498) are increased and become quant. when it is based on 2 : 4-dinitrophenylhydrazine (**I**) instead of on the quinone. 3 drops of a 1% solution of (**I**) in 2N-HCl are added to 1 or 2 drops of a MeOH or EtOH solution of >0·1 mg. of 2-methyl-1 : 4-naphthaquinone or related compound. After warming and cooling, 3 drops of aq. NH_3 (*d* 0·910) and 1 c.c. of $C_5H_{11}{\cdot}$OH are added. The green colour which appears separates in the $C_5H_{11}{\cdot}$OH phase when H_2O is added. 0·5 c.c. of 5% NaOMe in MeOH can replace the NH_3 and $C_5H_{11}{\cdot}$OH; the colour developed is then bluish-green. L. S. T.

1 : 4-Di(alkylamino)anthraquinones.—See B., 1941, II, 299.

1 : 8-Dihydroxy-2-methylanthraquinone. S. Shibata (*J. Pharm. Soc. Japan*, 1940, **60**, 201—202).—1 : 8-, new m.p. 296—297° (decomp.), or 1 : 5-dinitro-2-methylanthraquinone, new m.p. 343° (decomp.), is reduced (aq. Na_2S) to the $(NH_2)_2$-compound, new m.p. 203° or 213°, respectively, converted

(diazo-reaction) into the 1 : 8-, new m.p. 175° (diacetate, m.p. 205°), or 1 : 5-$(OH)_2$-compound, m.p. 187°, respectively. A. T. P.

Constituents of *Xanthoria fallax* (Hepp.), Arn. M. Asano and Y. Arata (*J. Pharm. Soc. Japan*, 1940, **60**, 206—208).—Chromatographic analysis shows that crude fallacin (*A*) (*ibid.*, 1936, **56**, 1007) is a mixture of fallacin (**I**), new m.p. 245—248° (triacetate, new m.p. 179—182°; *tripropionate*, m.p. 170—173°; *tribenzoate*, m.p. 230°; Me_3 ether, new m.p. 213—217°), with parietin (1 : 8-dihydroxy-6-methoxy-3-methylanthraquinone) (**II**) (A., 1925, i, 562) (*diacetate*, m.p. 188—189°; *dipropionate*, m.p. 162—163°). Oxidation (CrO_3 in AcOH–Ac_2O) of methylated (*A*) followed by methylation yields 3 : 1 : 4 : 5-OMe·$C_6H_2Me(CO_2Me)_2$ [derived from (**II**)] and (probably) 1 : 2 : 3 : 5-OMe·$C_6H_2(CO_2Me)_3$, showing that (**I**) is (probably) 1 : 8-dihydroxy-7-methoxy-3-hydroxymethylanthraquinone. A. Li.

III.—TERPENES.

Determination of unsaturation in the terpene series. L. M. Joshel, S. A. Hall, and S. Palkin (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 447—449).—The action of halogen, $KMnO_4$, or BzO_2H is unsatisfactory for determining unsaturation of terpenes. Quant. hydrogenation using either Pt or Pd catalyst in AcOH or high-pressure reduction with Raney Ni gives satisfactory results with a wide variety of terpenes but not with abietic or *l*-pimaric acid. J. D. R.

Optical activity and chemical constitution. V. Rotatory powers of camphoranilic acids, α- and β-naphthylcamphoramic acid at various degrees of neutralisation. M. Singh and A. Singh (*J. Indian Chem. Soc.*, 1941, **18**, 89—92; cf. A., 1936, 1383).—Determination of vals. of [α] of camphoranilic acid or β-naphthylcamphoramic acid, m.p. 212—214°, at various degrees of neutralisation with LiOH, NaOH, or KOH, shows that there is a gradual rise up to half-neutralisation point, then a sudden fall, followed by a continued rise in [α] until the acid is completely neutralised; no acid salt is isolated. 2′-, m.p. 193·5—194·5°, 3′-, m.p. 209°, and 4′-methylcamphoranilic acid, m.p. 212·5—214·5°, on addition of alkali, show a steady rise in [α] to a const., and then a continued rise to neutralisation point. α-Naphthylcamphoramic acid, m.p. 231·5—232·5°, behaves similarly. A. T. P.

Camphor series. VI. D. C. Sen (*J. Indian Chem. Soc.*, 1941, **18**, 76—80; cf. A., 1939, II, 120).—Dry CO_2 passed through sodio-*l*-thiocamphor (**I**) in C_6H_6–Et_2O at 0° and then at 39° gives d-*thiocamphor-α-carboxylic acid* (**II**), m.p. 125°, $[\alpha]_D^{30}$ +21·03° in C_6H_6 → +19·56° in 24 hr. (*Me* ester, m.p. 96°; semicarbazone, m.p. 133—134°, is identical with that derived from *d*-camphor-α-carboxylic acid). Sodio-*dl*-thiocamphor similarly affords the dl-α-*carboxylic acid*, m.p. 121°. The acids are decomposed by distillation at 95—100°/5 mm. to *l*- or *dl*-thiocamphor, respectively. The probable thio–thiol tautomerism of the acids may offer an explanation of the mutarotation of (**II**). (**I**)–CS_2–C_6H_6 at 0°, then at 80°, afford d-*thiocamphor-α-dithiocarboxylic acid*, m.p. 172°, $[\alpha]_D^{30}$ +58·03° in C_6H_6 (*semicarbazone*, m.p. 165°). (**I**)–CS_2–C_6H_6 at 0°, followed by Me_2SO_4 at 100°, yield *Me thiocamphor-α-dithiocarboxylate*, b.p. 80°/10 mm. (**I**) and HCO_2Et–C_6H_6 at 0° give *hydroxymethylenethiocamphor*, b.p. 110—115°/5 mm. (structures suggested) [*Cu*, m.p. 154—155° (decomp.), and *Hg*II salt, m.p. 125°, $[\alpha]_D^{30}$ +22·22° in C_6H_6; semicarbazone, m.p. 217—218°, identical with that from hydroxymethylenecamphor]. A. T. P.

Azulenes from *Ledum* camphor. G. A. Nyman and L. Mikander (*Snomen Kem.*, 1941, **14**, **B**, 3—4).—Ledol (also ledene and fractions of higher b.p. of *Ledum palustre* oil) gives on dehydrogenation with Se for 19 hr. at 270—280° Se-*ledum-azulene*, a blue-violet oil, and with S for 9 hr. at 155° S-*ledum-azulene*, a dark blue oil, purified via the additive *compounds* with *s*-$C_6H_3(NO_2)_3$, red-black needles, m.p. 146—147°, and blue-black needles, m.p. 152—153·5°, respectively. M. H. M. A.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin. III. Lignin of *Pawlonia imperialis*. K. Iwadare (*Bull. Chem. Soc. Japan*, 1941, **16**, 150—154).—*P. imperialis* wood contains 19·3% of lignin (OMe 20·7%) which contains both syringyl and guaiacyl radicals. Ethanolysis (2% EtOH–HCl) of the wood gives a product (OMe + OEt 26·9%) the C_6H_6 extract of which contains aldehydic (**I**) (6), acidic (1·5), phenolic (27), and neutral (3% of total lignin) fractions. (**I**) with NaOAc and 2% NaOH yields syringoyl Me ketone. Oxidation ($PhNO_2$ and 10% NaOH at 160° under pressure) of the wood yields aldehydes (38–43% of the lignin) containing syringaldehyde. A. Li.

Reaction for lignin.—See A., 1941, III, 714.

Saponins of the Chinese drug, San-chi, *Aralia bipinnatifida*. II. Arasaponin *B*. J. H. Chu and T. Q. Chou (*Chinese J. Physiol.*, 1941, **16**, 139—141; cf. A., 1937, II, 384).—Arasaponin *B* (**I**) is hydrolysed by HCl–EtOH to glucose and *arasapogenin* B, $C_{29}H_{52}O_3$, m.p. 247° (*acetate*, m.p. 216°). The formula $C_{23}H_{38}O_{10}$ for (**I**) is thus rendered doubtful. H. W.

Constituents of the seeds of *Zyzyphus vulgaris*, Lamark, var. *spinosus*, Bunge. R. Kawaguchi and K. W. Kim (*J. Pharm. Soc. Japan*, 1940, **60**, 171—174).—Treatment of the Et_2O extract of the seeds with light petroleum and then in Et_2O with 5% KOH gives the K salt of betulinic acid, decomp. 315—317° (corr.), which yields a *benzoate*, decomp. 341—344°, a *Me* ester, m.p. 223—225° (corr.) [*acetate*, m.p. 202—203°; *benzoate*, decomp. 248—250° (corr.)], *dihydrobetulinic acid*, decomp. 317—319° (corr.) {*acetate*, decomp. 308—310° (corr.) [*Me* ester, m.p. 237—239° (corr.)]}, and a *lactone*, $C_{30}H_{48}O_3$, decomp. 344—347° (corr.) [*acetate*, decomp. 357—360° (corr.) or 344—346° (corr.)]. The acetate, decomp. 290—292° (corr.), of the acid with Br in AcOH gives *dibromobetulinolactone acetate*, decomp. 290—291° (corr.) [293—296° (corr.)], but in Et_2O gives a Br_1-lactone; the acid gives no Br-lactone. The seeds yield also oleic, linoleic, myristic, palmitic, stearic, and behenic acid etc., sitosterol, and betulin, m.p. 251° (di-, m.p. 216°, and *mono-acetate*, m.p. 259—260°). Betulin gives *allobetulin*, m.p. 261° (*formate*, m.p. 311°), and *dihydrobetulin*, m.p. 270° (*diacetate*, m.p. 249—250°). R. S. C.

Lipins of tubercle bacilli. LXIV. Phleimycolic acid. R. L. Peck and R. J. Anderson (*J. Biol. Chem.*, 1941, **140**, 89—96).—The Me_2 ester (**I**), $[\alpha]_D$ +6·5° in $CHCl_3$, of phleimycolic acid, $C_{70}H_{138}O_6$ (from the timothy bacillus; cf. A., 1936, 311), when distilled under reduced pressure at 250—280° gives (73% yield) the Me ester, m.p. 55—56°, of a (? branched-chain) tetracosanoic acid, m.p. 75—76°, resembling that obtained from the firmly bound lipins of the leprosy bacillus (Geiger *et al.*, A., 1940, III, 170) and residual Me esters divisible into two fractions, m.p. 38—40° and 42—43°. The **I** val. (16·6) of (**I**) shows that it contains 30% of a saturated ester. A. Li.

V.—HETEROCYCLIC.

Addition of carboxylic acids to acetylene γ-glycols. J. S. Salkind and V. I. Baranov (*J. Gen. Chem. Russ.*, 1940, **10**, 1432—1434).—$(OH·CMe_2·C{:}{:}C)_2$, heated with $Hg(OAc)_2$ and BF_3 in AcOH (15—30 hr. at 110—115°), yields 3-keto-2 : 2 : 5 : 5-tetramethyl-2 : 3 : 4 : 5-tetrahydrofuran and 3-*acetoxy*-2 : 2 : 5 : 5-*tetramethyl*-2 : 5-*dihydrofuran*, m.p. 30·5—31°. R. T.

Synthesis of homo*iso*phytol and of an isoprene homologue of α-tocopherol. P. Karrer and K. S. Yap (*Helv. Chim. Acta*, 1941, **24**, 639—645).—Phytyl bromide is condensed with $CHAcNa·CO_2Et$ and the product is transformed by ketonic hydrolysis into *ζκξα-tetramethyl-Δ^ε-nonadecen-β-one* (**I**), b.p. 157°/0·3 mm., reduced (Pt in abs. EtOH) to the saturated *ketone*, b.p. 152—154°/0·2—0·25 mm. C_2H_2 and (**I**) give *γηλστ-pentamethyl-Δ^α-eikosin-γ-ol*, b.p. 160—164°/0·06 mm., reduced (Pt in abs. EtOH) to *γηλστ-pentamethyl-Δ^α-eikosen-γ-ol*, b.p. 154—157°/0·02 mm., which is transformed by PBr_3 into *α-bromo-γηλστ-pentamethyl-Δ^α-eikosene* [*homophytyl bromide*]. This condenses with trimethylquinol in boiling C_6H_6 containing anhyd. $ZnCl_2$ to *6-hydroxy-2 : 5 : 7 : 8-tetramethyl-2-δθμπ-tetramethylheptadecylchroman* [*homo-α-tocopherol*] (**II**) (*allophanate*, m.p. 161°). The vitamin-*E* activity of (**II**) is appreciably < that of α-tocopherol. Nevertheless it is biologically active in higher doses whereas the lower -*E* homologues in analogous amounts are completely ineffective. H. W.

Synthesis of 7-hydroxy-5-methylcoumarin. K. R. Rao and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **A**, **13**, 255—258).—Orcinol and $Zn(CN)_2$–HCl–Et_2O at 0°, followed by

decomp. of the aldimine hydrochloride with H_2O, afford 1 : 3 : 5 : 6-$C_6H_2Me(OH)_2$·CHO, which condenses with $CH_2(CO_2Et)_2$–piperidine at 0°, then at room temp., to *Et 7-hydroxy-5-methylcoumarin-3-carboxylate*, m.p. 193—194°. The latter is hydrolysed by 8% aq. NaOH at room temp. (3 days) to the *3-carboxylic acid*, m.p. 240° (decomp.). which with Cu-bronze in quinoline at 150—160° gives *7-hydroxy-5-methylcoumarin*, m.p. 247—248°, identical with that obtained from orcinol and malic acid. A. T. P.

Fluorescence of certain coumarin derivatives. S. Rangaswami, T. R. Seshadri, and V. Venkateswarlu (*Proc. Indian Acad. Sci.*, 1941, **A**, **13**, 316—321; cf. A., 1941, II, 107).—2 : 4 : 1-OH·C_6H_3(OMe)·CHO and $CH_2Ac·CO_2Et$, $CH_2Bz·CO_2Et$, or $CH_2(CO_2Et)_2$ in EtOH–piperidine yield *7-methoxy-3-acetyl-*, m.p. 168—169°, or *-benzoyl-coumarin*, m.p. 153°, or *Et 7-methoxycoumarin-3-carboxylate*, m.p. 134° (and thence the *carboxylic acid*, m.p. 195°). Similarly prepared from 1 : 3 : 5 : 6-$C_6H_2Me(OH)_2$·CHO are *7-hydroxy-3-acetyl-* (+0·5H_2O), m.p. 224—225°, and *-benzoyl-5-methylcoumarin*, m.p. 231—232°, and from 2 : 4 : 1-$C_6H_3(OH)_2$·CHO, *7-hydroxy-3-benzoylcoumarin*, m.p. 236—237°. Colours of the fluorescence of the compounds in H_2SO_4, EtOH, or in EtOH + 1 drop of dil. H_2SO_4 or NaOH are given; CO_2Et, CO_2H, or Ac in position 3 of 7-hydroxy- and -methoxy-coumarins (blue or violet fluoresence respectively) enhances the fluorescence so much that it is bright even in neutral EtOH solution; the 3-Bz derivatives exhibit no visible fluorescence. Theoretical considerations are discussed. A. T. P.

Synthesis of 6 : 8-dimethoxy-3-alkyl*iso*coumarins. I. Alkylidenephthalide derivatives. II. 6 : 8-Dimethoxy-3-methyl*iso*coumarin. H. Nogami (*J. Pharm. Soc. Japan*, 1941, **61**, 21—24, 24—26).—I. 3-Ethylidenephthalide and NO_2–C_6H_6 at 0—40° [then AcOH at 100° (bath)] yield 3-(α-nitroethylidene)phthalide, m.p. 124°, converted by HI–P or Zn–Hg–aq. HCl (1 : 1) into 3-methyl*iso*coumarin, m.p. 73—74°; 3-(α-nitropropylidene)phthalide, m.p. 141—143°, affords 3-ethyl*iso*coumarin, m.p. 76—77°. 3 : 5-Dimethoxyphthalic anhydride (**I**), $BuCO_2Na$, and $(BuCO)_2O$ at 185—210° (2 hr.) afford 5 : 7-*dimethoxy-3-butylidenephthalide* (Me ether of laboritonide), m.p. 99° [HCl–$COMe_2$ at 50° gives 3 : 5-*dimethoxyvalerophenone-2-carboxylic acid* (Me ether of laboritonic acid), m.p. 134°], and 4 : 6-*dimethoxy-3-butylidenephthalide*, m.p. 126—127°. The latter yields (HCl–$COMe_2$) 2 : 4-dimethoxyvalerophenone-6-carboxylic acid, decarboxylated by Cu-bronze–quinoline at 200° to 2 : 4-*dimethoxyvalerophenone*, m.p. 38·5°, also obtained by methylation (MeI–K_2CO_3) of 2 : 4-*dihydroxyvalerophenone*, m.p. 63° (*semicarbazone*, m.p. 175°), prepared from *o*-$C_6H_4(OH)_2$, $BuCO_2H$, and $ZnCl_2$. (**I**), $(EtCO)_2O$, and $EtCO_2Na$ at 170—180° afford 5 : 7-*dimethoxy-*, m.p. 145° (3 : 5-*dimethoxypropiophenone-2-carboxylic acid*, m.p. 158°, gives 3 : 5-dimethoxypropiophenone), and 4 : 6-*dimethoxy-3-ethylidenephthalide*, m.p. 185° (and thence 2 : 4-*dimethoxypropiophenone-6-carboxylic acid*, m.p. 160°, and 2 : 4-dimethoxypropiophenone, m.p. 75°).

II. 6-Et H 5-carbethoxymethylresorcinol-2 : 6-dicarboxylate and Cu-bronze–quinoline at 190—195° afford *Et*$_2$ 4 : 6-*dihydroxyhomophthalate*, m.p. 108°; its *Me*$_2$ *ether*, b.p. 180°/2 mm., and KOEt–EtOH give 3 : 5-*dimethoxy-2-carbethoxyphenylacetic acid*, m.p. 103° [chloride (**II**); *amide*, m.p. 105·5°]. (**II**) and CHNaAc·CO_2Et–EtOH yield *Et* γ-(3 : 5-*dimethoxy-2-carbethoxyphenyl)acetoacetate*, m.p. 38·5° [*p-nitrophenylhydrazone*, m.p. 123°; *p*-$NO_2·C_6H_4·NH·NH_2$–aq. AcOH–EtOH yield *1-phenyl-3-(2′-carbethoxy-3′ : 5′-dimethoxyphenyl)-methyl-5-pyrazolone*, m.p. 168—169° (decomp.)], converted by KOEt–EtOH into *2-carboxy-3 : 5-dimethoxybenzyl Me ketone*, m.p. 139—141° [*p-nitrophenylhydrazone*, m.p. 197° (decomp.)], and thence (HCO_2H) 6 : 8-*dimethoxy-3-methyl*-iso*coumarin*, m.p. 155·5° (NH_3 gives the -iso*carbostyril*, m.p. 216—218°). A. T. P.

Condensation of *C*-acetylmethone with aromatic aldehydes. B. H. Iyer (*J. Indian Inst. Sci.*, 1941, **23**, **A**, 175—182).—*C*-Acetylmethone (**I**) [*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 315—320° (decomp.)] and PhCHO condense (NaOH–EtOH) to *5-hydroxy-7 : 7-dimethyl-7 : 8-dihydroflavanone*, m.p. 99° [*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 220—225° (decomp.)], which adds Br in boiling CS_2 solution, giving the *pentabromide*, m.p. 178°. The properties of the substance indicate its structure and also that (**I**) has a true Ac structure. 2′ : 5-*Dihydroxy-*, m.p. 150—151°, 2′-*methoxy-*, m.p. 105—107°, 4′-*methoxy-*, m.p. 132—133°, and 5-*hydroxy-3′ : 4′-methylenedioxy--7 : 7-dimethyl-7 : 8-dihydroflavanone*, m.p. 115° [*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 215—218°, 237—240°, 195—200°, and m.p. 215—216° respectively (all decomp.)], are also described. F. R. S.

Constituents of *Equisetum arvense*, L. H. Nakamura and G. Hukuti (*J. Pharm. Soc. Japan*, 1940, **60**, 179—180).—The aërial stems of *E. arvense*, L., yield *iso*quercitin, +4H_2O, m.p. 220—221° (hydrolysed to quercitrin and glucose), luteolin 5-glucoside, +3H_2O, m.p. 260—263° [hydrolysed to luteolin and glucose; methylation and then hydrolysis gives 5-hydroxy-7 : 3′ : 4′-trimethoxyflavone, m.p. 162° (Barger, A., 1924, i, 355)], and *equisitrin*, $C_{27}H_{30}O_{16}$, +2H_2O, m.p. 195—196°, shown to be *kaempherol 7-diglucoside* by hydrolysis to kaempherol and glucose (2 mols.) and conversion by CH_2N_2, and then 5% H_2SO_4 into *7-hydroxy-3 : 5 : 4′-trimethoxyflavone*, m.p. 283—285° (*acetate*, m.p. 204—205°), which is synthesised from 1 : 3 : 5-$(OH)_2C_6H_2$·OMe by way of 5 : 1 : 3 : 4-OMe·C_6H_2(OMe)·CO·CH_2·OMe. R. S. C.

Constituents of *Persicaria hydropiper*. III. R. Kawaguchi and K. W. Kim (*J. Pharm. Soc. Japan*, 1940, **60**, 174—175).—Persicarin with CH_2N_2–MeOH gives a substance, m.p. 175°, which in 1% HCl yields 5 : 7 : 3′ : 4′-tetramethylquercitin. It is thus *3′-methyl-3-quercitinyl K sulphate*. R. S. C.

Formation of oxonium compound of dioxan with arsenic trichloride. M. S. Malinovski (*J. Gen. Chem. Russ.*, 1940, **10**, 1202).—Dioxan in Et_2O and $AsCl_3$ yield an *oxonium* compound (1 : 1), m.p. 66—68°. R. T.

Attempts towards synthesis of cantharidin. III. Condensation of ethyl 3 : 4-diketotetrahydrofuran-2 : 5-dicarboxylate with α-bromo-esters. B. H. Iyer and P. C. Guha (*J. Indian Inst. Sci.*, 1941, **23**, **A**, 159—167).—Condensation of the Na_2 derivative of Et_2 3 : 4-diketotetrahydrofuran-2 : 5-dicarboxylate with $CH_2Br·CO_2Et$ gives *Et*$_2$ 3 : 4-*dicarbethoxymethoxyfuran-2 : 5-dicarboxylate*, m.p. 65°, which on saponification affords the *K* salt of the tetracarboxylic acid and on acid hydrolysis (cold conc. HCl) yields *Et*$_2$ 3 : 4-*dicarboxymethoxyfuran-2 : 5-dicarboxylate* (+H_2O), m.p. 221—225° (decomp.). The products obtained with the reaction on Et 2 : 5-diketotetrahydrothiophen-3 : 4-dicarboxylate are *Et*$_2$ 3 : 4-*dicarbethoxymethoxythiophen-2 : 5-dicarboxylate*, m.p. 50°, the *K* salt of the tetracarboxylic acid, and *Et*$_2$ 3 : 4-*dicarboxymethoxythiophen-2 : 5-dicarboxylate*, m.p. 225—227° (decomp.). F. R. S.

Synthesis of substances related to the sterols. XXXIV. (Miss) N. A. McGinnis and (Sir) R. Robinson (*J.C.S.*, 1941, 404—408; cf. A., 1938, II, 145).—β-Chloropropionacetal (**I**) and $COMe·[CH_2]_2$·Cl (**II**) in K_2S–EtOH afford *bis-γ-ketobutyl sulphide* (**III**), b.p. 108—114°/1—2 mm. (*semicarbazone*, m.p. 227—228°, corresponds with an anhydro-derivative, *i.e.*, of 3-acetyl-4-methyl-Δ^3-dihydrothiopyran). (**II**) and γγ-diethoxypropanethiol in KOEt–EtOH also afford (**III**) (*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 150—152°). (**I**) and K_2S–EtOH yield *bis-γγ-diethoxypropyl sulphide*, b.p. 130—132°/0·27 mm., converted by N-H_2SO_4 into Δ^3-*dihydrothiopyran-3-aldehyde*, m.p. 226—228° (2 : 4-*dinitrophenylhydrazone*, m.p. 247—248°), and thence by MgMeI into 3-(α-*hydroxyethyl*)-Δ^3-*dihydrothiopyran*, b.p. 119—120°/4—5 mm., which with $Al(OBu^{\gamma})_3$–C_6H_6 at 60—65° yields 3-acetyl-Δ^3-dihydrothiopyran (**IV**), b.p. 95—103°/1—3 mm. (*semicarbazone*, m.p. 227—228°). 6-Methoxy-α-tetralone refluxed in dry N_2 with $NaNH_2$–Et_2O and treated with (**IV**) in Et_2O at 0° to room temp. gives *3-keto-7-methoxy-1 : 2 : 3 : 9 : 10 : 11 : 5′ : 6′-octahydrothiopyrano*(4′ : 3′ : 1 : 2)*phenanthrene* (**V**), two stereoisomerides, (*a*), m.p. 234—236° [2 : 4-dinitrophenylhydrazone, m.p. 268° (decomp.)], and (*b*), m.p. 190—194° [2 : 4-dinitrophenylhydrazone, m.p. 250° (decomp.)], and possibly a third isomeride. (*a*) and HI (*d* 1·7)–AcOH at 130—140° for 10 min. afford the 7-*OH*-compound, decomp. >240°; (*a*) is oxidised (H_2O_2–AcOH at room temp.) to the corresponding *dioxide*, m.p. 279—281°, or is reduced (Na–*iso*-C_5H_{11}·OH) to *3-hydroxy-7-methoxy-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12 : 5′ : 6′-decahydrothiopyrano*(4′ : 3′ : 1 : 2)*phenanthrene*, m.p. 179—181° (no ketonic reactions), which is converted by $Al(OPr^{\beta})_3$–PhMe–*cyclo*hexanone (reflux) into the *3-keto-7-methoxy*-compound, m.p. 192—193° [*semicarbazone*, m.p. 239—241° (decomp.); 2 : 4-dinitrophenylhydrazone]. The latter is *C*-methylated by MeI–K–Bu$^{\gamma}$OH (reflux) to *3-keto-7-methoxy-2-methyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12 : 5′ : 6′-decahydrothiopyrano*-(4′ : 3′ : 1 : 2)*phenanthrene*, m.p. 156—157° (dinitrophenylhydrazone). Bis-γ-hydroxypropyl sulphide (**VI**) (phenyl-

urethane, new m.p. 122—123°) affords [NaOAc–Ac_2O at 100° (bath)] a *diacetate*, b.p. 229—234°/0·6 mm., converted by $KMnO_4$–$COMe_2$ in the cold into *bis-γ-acetoxypropyl sulphone*, m.p. 53—55°, which with aq. NaOH–EtOH affords an oil, b.p. 140—142°/0·5 mm., probably (**VI**). A. T. P.

Thioacyl derivatives of 2-aminopyridine. I. L. Knuniantz and D. A. Katrenko (*J. Gen. Chem. Russ.*, 1940, **10**, 1167—1170).—2-Acetamidopyridine and P_2S_5 in boiling xylene yield *2-thioacetamidopyridine* (**I**), m.p. 108° [*Na* salt, m.p. 100—106°; *S-Me ether*, b.p. 123—129°/28 mm. (*methiodide*, m.p. 169—170°)], not oxidised by $K_3Fe(CN)_6$ or H_2O_2. *2-Thiobenzamidopyridine*, m.p. 113—114°, is prepared similarly to (**I**). R. T.

Pyridine series. I. Synthesis of 3-hydroxy-2-methylpyridine-4 : 5-dicarboxylic acid. A. Ichiba and S. Emoto (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1941, **38**, 347—352; cf. A., 1939, II, 487).—Et 3-cyano-6-methyl-2-pyridone-4-carboxylate (cf. Bardhan, A., 1929, 1462) with fuming HNO_3 in Ac_2O below 50° gives *Et 5-nitro-3-cyano-6-methyl-2-pyridone-4-carboxylate*, m.p. 193°, which heated for 3—4 hr. with PCl_5 and PhCl yields *Et 2-chloro-5-nitro-3-cyano-6-methylpyridine-4-carboxylate*, m.p. 60·5—61·5° (sublimes at 110—140°/10^{-4} mm.), reduced (H_2–PtO_2, Sn–HCl, or $SnCl_2$–HCl) to the 5-NH_2-compound (**I**), m.p. 171—172°. (**I**) with H_2–Pd–$BaCO_3$ at atm. pressure absorbs 2 H, giving *Et 5-amino-3-cyano-2-methylpyridine-4-carboxylate*, m.p. 131·5—132·5°, which with conc. HCl at 135° for 3 hr. and then at 160° for 0·5 hr. yields *3-amino-2-methylpyridine-4 : 5-dicarboxylic acid monohydrate*, m.p. 241—242° (decomp.); the diazo-solution of this when heated gives *3-hydroxy-2-methylpyridine-4 : 5-dicarboxylic acid*, m.p. 258—259° (decomp.). J. L. D.

2-*p*-*p*'-Aminobenzenesulphonamidobenzenesulphonamidopyridine.—See B., 1941, III, 216.

Synthesis of 3-indolylacetic acid. I. J. Tanaka (*J. Pharm. Soc. Japan*, 1940, **60**, 17—19).—2-Carboxy-3-indolylacetic acid and HCl–MeOH give the *Me* (**I**), m.p. 186°, with a little Me_2 ester, m.p. 128°. Decarboxylation of (**I**), best (50%) by Cu chromite in quinoline at 150—190°, gives 3-indolylacetic acid, m.p. 165—166°. R. S. C.

Sulphanilamides of pyridine and quinoline type.—See B., 1941, III, 245.

Quinaldines.—See B., 1941, II, 255.

Synthesis of demethoxylated Plasmoquin, 8-[*N*-(δ-diethylamino-α-methyl)butyl]aminoquinoline. G. V. Tschelincev and B. M. Dubinin (*J. Gen. Chem. Russ.*, 1940, **10**, 1395—1398).—δ-Amino-α-diethylaminopentane in aq. SO_2 and 8-hydroxyquinoline condense (30 hr. at the b.p.), to *8-[N-(δ-diethylamino-α-methyl)butyl]aminoquinoline*, b.p. 171—172°/1·5 mm. [*dipicrate*, m.p. 150°; *N-Ac* derivative, b.p. 195—196°/1·5 mm. (*picrate*, m.p. 136—138°); *5-Cl*-derivative, b.p. 180—181°/1·5 mm. (*dipicrate*, m.p. 136°); *5-Br*-derivative, b.p. 198—201°/1·5 mm. (*dipicrate*, m.p. 121—122°)]. R. T.

Reaction of diazo-compounds with indophenols. J. S. Joffe and B. K. Kritschevtzov (*J. Gen. Chem. Russ.*, 1940, **10**, 1385—1390).—3-Benzoquinoneiminocarbazole in AcOH and *p*-$SO_3H{\cdot}C_6H_4{\cdot}N_2Cl$ or *p*-$C_6H_4Cl{\cdot}N_2Cl$ yield *3-[2'(5')-p-sulphophenylbenzoquinone]*- and *3-(2' : 5'-di-p-sulphophenylbenzoquinone)*-, or *3-[2'(5')-p-chlorophenylbenzoquinone]*- and *3-(2' : 5'-di-p-chlorophenylbenzoquinone)-iminocarbazole*. R. T.

Synthesis of new acridine antimalarials. I. L. Knuniantz and Z. V. Benevolenskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 1415—1417).—2 : 4-$C_6H_3Cl_2{\cdot}CO_2H$ and 3-nitro-4-aminoanisole yield *3-chloro-6'-nitro-4'-methoxydiphenylamine-6-carboxylic acid*, m.p. 268—269°, which with $POCl_3$ (5 hr. at 120—130°) affords *5 : 8-dichloro-1-nitro-3-methoxyacridine*, m.p. 272—273°, and this, heated with PhOH, gives *8-chloro-1-nitro-5-phenoxy-3-methoxyacridine*, m.p. 220—222°. This condenses with β-amino-ε-diethylaminopentane (1 hr. at 130°) to *8-chloro-1-nitro-5-(δ-diethylamino-α-methylbutyl)amino-3-methoxyacridine* (**I**), reduced ($SnCl_2$ in conc. HCl) to the corresponding 1-NH_2-compound (**II**) (*trihydrochloride*, m.p. 245—247°), which with $NEt_2{\cdot}[CH_2]_3{\cdot}Cl$ (2 hr. at 130—140°, then 3 hr. at 150—160°) affords *8-chloro-1-(γ-diethylaminopropyl)-amino-5-(δ-diethylamino-α-methylbutyl)amino-3-methoxyacridine tetrahydrochloride* (**III**), m.p. 181—184°. (**I**) has a feeble antimalarial action, whilst (**II**) and (**III**) are inactive in this respect. R. T.

Acridine derivatives. VII. Compounds with mercury, copper, and antimony. S. J. Das-Gupta (*J. Indian Chem. Soc.*, 1941, **18**, 93—96; cf. A., 1940, II, 263).—5-Chloroacridine and K xanthogenate at 120—130° afford *5-thiolacridine*, m.p. 247—249° (yellow enolic and red ketonic form) (*Au*, m.p. 288—290°, and *Ag* salt, m.p. 278—280°), converted by $HgCl_2$ and $HgNO_3$ into *mercurodi-5-thiolacridine*, m.p. 298—300° (decomp.), and *5-mercurothiolacridine*, m.p. 293—294° (decomp.), respectively, or by $CuSO_4$–aq. EtOH–NaOH into basic *cuprodi-5-thiolacridine*, m.p. 284—288° (decomp.), $(C_{13}H_8NS)_2Cu,CuO$. 2-Chloro-7-methoxy-5-thiolacridine (**I**) with $HgCl_2$, $HgNO_3$, or $CuSO_4$, in aq. EtOH–NaOH, yields *mercurodi-5-thio-*, m.p. 284—285° (red and yellow allotropic modifications), *5-mercurothio-*, m.p. 307—308°, and *cuprodi-5-thio-(2-chloro-7-methoxy)acridine*, m.p. 291—293° (decomp.) (+4H_2O, not lost at 120°, but partly lost at 150°). (**I**) and Na antimonyl tartrate in aq. EtOH–NaOH afford *antimonyl-5-thio-(2-chloro-7-methoxy)acridine*, m.p. 256° (orange-yellow and red allotropic modifications). 7-Methoxy-5-thiolacridine gives *mercurodi-5-thio-*, m.p. 254°, *5-mercurothio-*, m.p. 244—245°, and *cuprodi-5-thio-(7-methoxy)acridine*, m.p. 313—314° (decomp.). A. T. P.

Constitution of antipyrine and related compounds. V. Experimental proof of the third form (third oscillation formula) of antipyrines. VI. Molecular state of antipyrine and the new "oscillation state" theory of the molecule. R. Kitamura (*J. Pharm. Soc. Japan*, 1940, **60**, 3—9, 9—17; cf. A., 1939, II, 450).—V. Betaines, $CR\lessdot^{N^+R'{\cdot}NR''}_{CH=C{\cdot}O^-}$ (*A*) and $CR\lessdot^{NR''{\cdot}N^+R'}_{CH-C{\cdot}O^-}$ (*B*), are identical if R' = R''. 5-Hydroxy-1 : 3-dimethylpyrazole [prep. from $NH_2{\cdot}NHMe$ and $CH_2Ac{\cdot}CO_2Et$ (**I**)], m.p. 113—117° (lit. 100—105°), and MeI at 100° give 3-hydroxy-1 : 2 : 5-trimethylpyrazolinium betaine (**II**) (form *A*), m.p. 40—45°, b.p. 186—190°/25—26 mm. $(CO{\cdot}NH{\cdot}NHMe)_2$, (**I**), and PCl_3 give 3-hydroxy-1 : 5-dimethylpyrazole, m.p. 172—173°, which with MeI gives (**II**) (form *B*). (**II**) is also obtained from 3-hydroxy-5-methylpyrazole (for which four forms are possible) by MeI and as follows: 3(5)-chloro-5(3)-methylpyrazole and MeI give 3-chloro-1 : 2 : 5-trimethylpyrazolinium iodide (2 forms), converted by KSH into the thiolbetaine (2 forms), which with H_2O_2 gives (**II**).

VI. Betaines (*A*) and (*B*) are in equilibrium with each other and the 3-keto-1 : 2 : 5-trialkyl-Δ^4-pyrazoline (*C*). Identity of these three forms is due to the mol. existing in a "state of oscillation," which consists of continual cyclic isomerisation, thus: $A \rightarrow B \rightarrow C \rightarrow A$ etc. At no time is the mol. stationary in any one form and the conception thus differs from (*a*) classical theory, according to which forms have actual, if momentary, existence at the end of each "half-oscillation," and (*b*) resonance, according to which the mol. is stationary in an intermediate form. The movement of electrons is accompanied by movement of nuclei and the energy of these movements (termed "half-oscillation energy") is equiv. to "resonance energy." R. S. C.

Aminomethyleneamino-1 : 3 : 5-triazines.—See B., 1941, II, 256.

5-*p*-Nitrobenzenesulphonamidotetrazole.—See B., 1941, III, 246.

Mercuriphenyl derivatives of ureides.—See B., 1941, III, 218.

Structure of the mesomorphic phase of certain cyanine dyes. S. E. Sheppard (*Science*, 1941, **93**, 42—43).—A structure is proposed for the aggregated phase of diethyl-ψ-cyanine and related dyes which give a new absorption and fluorescence band named a *Z*-band; the corresponding aggregation of the dye is named the *Z*-state. The structure proposed postulates linkings of H_2O mols. co-ordinated intermolecularly between opposite terminal N atoms of parallel resonance chains. These intermol. resonance linkings through "hydrate" H_2O mols. are supposed to furnish the characteristic *Z*-band on excitation by light. L. S. T.

Action of diazomethane on hippuryl chloride. P. Karrer and G. Bussmann (*Helv. Chim. Acta*, 1941, **24**, 645—646; cf. A., 1925, i, 593).—CH_2N_2 and hippuryl chloride give *2-phenyloxazolone*, converted by PhCHO, NaOAc, and warm Ac_2O into 2-phenyl-4-benzylideneoxazolone, m.p. 165°. H. W.

Molecular compounds of the sulphanilamide series. I. S. Kuroyanagi (*J. Pharm. Soc. Japan*, 1940, **60**, 176—177).—By the thaw point–m.p. method it is shown that *p*-

$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ gives a 1 : 1 additive *compound*, thaw point 112°, m.p. 126·5°, with 2-thiol-4-methylthiazole (**I**), but not with $CO(NH_2)_2$, $CO(NH{\cdot}COEt)_2$ (**II**), quinine, 4-phenylthiazole, salicylic (**III**) or hippuric acid (**IV**), or *p*-$NO_2{\cdot}C_6H_4{\cdot}OH$ (**V**). 2-Sulphanilamidopyridine gives 1 : 1 additive *compounds* with (**I**), thaw point 143°, m.p. 156·5°, and (**V**), thaw point 136°, m.p. 146°, but not with (**II**), (**III**), or (**IV**). *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}SO_2{\cdot}NMe_2$-*p* gives no such compound with (**I**), (**II**), (**IV**), or (**V**). R. S. C.

2-*p*-Aminobenzenesulphonamido-4-methylthiazole.—See B., 1941, III, 216.

Chlorothiolbenzthiazoles.—See B., 1941, II, 255.

Synthesis of *C*-methyl derivatives of some medicaments. I. Synthesis of 4-methyl- and 3 : 4-dimethyl-*iso*quinolines. II. Synthesis of dimethyleocaine, *p*-(3 : 4-dimethylcinnamoyloxy)phenylcarbamide, and 4 : 5-dimethyl-*o*-phthaltetraethyldiamide. S. Sugasawa and N. Sugimoto (*J. Pharm. Soc. Japan*, 1941, **61**, 26—28, 29—30; cf. A., 1939, II, 283).—I. β-3 : 4-Dimethoxyphenyl-β-methylpropionic acid and dry NH_3 at 210—225° afford the *amide*, m.p. 126—127·5°, converted by NaOCl at 70° (followed by aq. NaOH at 80°) into β-3 : 4-*dimethoxyphenylpropylamine*, b.p. 150—152°/10 mm. (*hydrochloride*, m.p. 205°), and thence by veratroyl chloride in $COMe_2$–Na_2CO_3 into β-3 : 4-*dimethoxyphenyl* (3′ : 4′-*dimethoxybenz*)-n-*propylamide*, m.p. 145°, which with $POCl_3$–PhMe at 130° gives 6 : 7-*dimethoxy*-1-(3′ : 4′-*dimethoxyphenyl*)-4-*methyl*-3 : 4-*dihydro*isoquinoline, dehydrogenated (method : Akabori *et al.*, A., 1929, 1170) to the -4-*methyl*isoquinoline, m.p. 161—162°. β-(3 : 4-*Dimethoxyphenyl*)*homoveratro*-n-*propylamide*, m.p. 172·5°, affords 6 : 7-dimethoxy-1-(3′ : 4′-dimethoxybenzyl)-4-methyl-3 : 4-dihydro*iso*quinoline (*picrate*, m.p. 103°). The following are prepared similarly : 3 : 4-*dimethoxy*-αβ-*dimethylcinnamamide*, m.p. 136°; β-3 : 4-*dimethoxyphenyl*-αβ-*dimethylethylamine*, b.p. 152—153°/9 mm. (*hydrochloride*, m.p. 202—203°); β-3 : 4-*dimethoxyphenyl*-3′ : 4′-*dimethoxybenzethylamide*, m.p. 121—122°; 6 : 7-*dimethoxy*-1-(3′ : 4′-*dimethoxyphenyl*)-3 : 4-*dimethyl*-3 : 4-*dihydro*isoquinoline, m.p. 206—207° (*picrate*, m.p. 186—187°), and -3 : 4-*dimethyl*isoquinoline, m.p. 159—160°.

II. 3 : 4 : 1-$C_6H_3Me_2{\cdot}CHO$, m.p. 228°; and $CH_2(CO_2H)_2$–C_5H_5N + piperidine yield 3 : 4-dimethylcinnamic acid, new m.p. 172°; the corresponding chloride, b.p. 138—140°/5 mm., is converted by *p*-hydroxyphenylcarbamide in C_5H_5N–Et_2O into p-3 : 4-*dimethylcinnamoyloxyphenylcarbamide*, m.p. 206°. 4 : 5 : 1 : 2-$C_6H_2Me_2(CO)_2O$, m.p. 206°, and $NHEt_2$ at room temp., then at 100° (bath), afford 4 : 5-*dimethylphthal-mono-*, m.p. 167°, and thence (through the chloride) *-bis-diethylamide*, m.p. 62°. 3 : 4 : 1-$C_6H_3Me{\cdot}COCl$ and ecgonine Me ester in xylene afford *dimethylcocaine*, m.p. 92°, $[\alpha]_D^{19}$ −18·02° in MeOH [*hydrochloride*, m.p. 193° (decomp.)]. A. T. P.

Salts of alkaloids with bromo-complexes of some heavy metals. E. P. White (*J. Amer. Pharm. Assoc.*, 1941, **30**, 156—161).—The following *complexes* were prepared : type BCdBr$_4$ where B = quinine (**I**), cinchonine (**II**), cinchonidine, and sparteine (**III**), m.p. 265°, 256°, 226°, and 238°, respectively; type B_2CdBr$_4$ where B = brucine (**IV**), tropacocaine (**V**), narcotine, hydrastinine, and cotarnine, m.p. 218°, 228°, 227°, decomp. 120°, and 202°, respectively; type B_3,2CdBr$_4$ where B = veratrine (**VI**), m.p. 261°; type BHgBr$_4$ where B = (**I**), (**II**), and (**III**), m.p. 257°, 246°, and 278°, respectively; type B_2HgBr$_4$ where B = (**IV**), m.p. 233°; type BPbBr$_2$ where B = (**V**), decomp. 265°; type B_2PbBr$_4$ where B = (**IV**), m.p. 230—260°; type BBiBr$_5$ where B = (**I**), m.p. 210—230°; type B_2BiBr$_5$ where B = (**IV**), m.p. 273°, and (**VI**); type BSbBr$_5$ where B = (**I**) and (**IV**), decomp. 50—60° and 186—197°, respectively. All m.p. are with slight decomp. F. O. H.

VI.—ORGANO-METALLIC COMPOUNDS.

Reaction of aminophenylarsinic acids with furfuraldehyde. V. I. Kuznetzov and N. A. Vasiunina (*J. Gen. Chem. Russ.*, 1940, **10**, 1203—1209).—*o*-$NH_2{\cdot}C_6H_4{\cdot}AsO_3H_2$ and furfuraldehyde in aq. HCl yield *o-furfurylideneaminophenylarsinic acid*, decomp. 166—167°; the *m*- and *p*-isomerides do not react under these conditions. When the reagents are added to aq. NaOH, and the solution acidified with HCl, *dyes* $NHR{\cdot}CH{:}CH{\cdot}CH{:}C(OH){\cdot}CH{:}NR,HCl$ (R = *o*-, *m*-, and *p*-$C_6H_4{\cdot}AsO_3H_2$) are produced. R. T.

Condensation products of organo-silane diols. J. F. Hyde and R. C. Delong (*J. Amer. Chem. Soc.*, 1941, **63**, 1194—1196).—By hydrolysis and subsequent atm. oxidation of diethyl- (**I**), dimethyl- (**II**), diphenyl-, phenyl-ethyl- and -methyl-dichlorosilanes, liquid and resinous condensation products have been isolated. (**I**) and (**II**) yield cyclic trimerides. Cryst. *cyclic diphenyltrisiloxane*, m.p. 199·5—200°, is described. The reactions involved in the condensations are briefly discussed. W. R. A.

VII.—PROTEINS.

Crystalline insulin derivatives. E. H. Lang and L. Reiner (*Science*, 1941, **93**, 401).—Insulin-*p*-azobenzenesulphonic acids (**I**) and insulin-*p*-azobenzyltrimethylammonium chlorides (**II**) yield perfectly-shaped rhombohedral crystals when ≯ 6 groups are coupled to 1 mol. of insulin. (**I**) containing 10 and 15 groups give deformed ellipsoid-shaped crystals only, whilst (**II**) containing 15 groups failed to crystallise. Insulin-*p*-azoiodobenzene and insulin-*p*-azophenylarsinic acid have been prepared in a cryst. form suitable for *X*-ray examination. L. S. T.

Proteins. W. Harrison (*Chem. and Ind.*, 1941, 558—559).—The formula for α-proteins proposed by Astbury (A., 1941, II, 274) is criticised on the ground of insufficient experimental evidence. The high elasticity of wet proteins is a factor independent of changes in the *X*-ray spectrum, and cannot be accepted as evidence for 100% mol. extensibility of the α-protein. Other ways in which the changes in the *X*-ray spectrum could be explained are mentioned. A. J. M.

***X*-Ray analysis of protein denaturation.** M. Spiegel-Adolf and G. C. Henny (*J. Physical Chem.*, 1941, **45**, 931—937).—Comparative *X*-ray examinations of heat-denatured and ultraviolet light-denatured horse serum-albumin indicate that differences exist between the two products of denaturation. Samples denatured by ultra-violet light show practically no difference in their diffraction patterns from undenatured samples. Samples denatured by both methods give patterns identical with those given by samples denatured by heat only. The changes observed in heat-denatured samples are not reversible on contact with H_2O alone, but reversal occurs with other treatments. C. R. H.

Solubility as a criterion of purity of proteins.—See A., 1941, III, 704.

Phosphopeptone of casein (lactotyrine). T. Posternak and H. Pollaczek (*Arch. Sci. phys. nat.*, 1940, [v], **22**, *Suppl.*, 236—239).—Tryptic digestion (3—4 days) of casein yields phosphopeptone-I (N/P = 3·4—3·6), which on prolonged digestion yields phosphopeptone-II (N/P = 2·3; NH_2-N = 14·3% of total N), which is a heptapeptide esterified with 3 H_3PO_4 and containing serine (3 mols.), glutamic acid, and a little *iso*leucine. After treatment with HNO_2 followed by acid hydrolysis, -II gives glyceric acid, indicating that the terminal NH_2-group belongs to serine. -I and -II with kidney-phosphatase lose ⅔ of and all the combined P, respectively. Partly dephosphorylated -I and -II are hydrolysed by aminopolypeptidase (pig intestine) so that the increase in NH_2-N equals the increase in inorg. P. Hence -I and -II must have two adjacent phosphoseryl radicals at one end of the chain and a terminal serine group, and -I must have three phosphoseryl residues, two being adjacent and terminal and one sandwiched between other NH_2-acid residues. J. L. D.

Denaturation of sericin. IV. Relation of denaturation of $\alpha_{3\cdot8}$-sericin and $\alpha_{4\cdot4}$-sericin.—See A., 1941, III, 771.

VIII.—ANALYSIS.

Micro-method for the identification of volatile liquids. Vapour pressures of *cyclo*pentane and the pentenes. S. W. Benson (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 502—504).—An apparatus is described for measuring the mol. wt., v.p. over a range of temp., and *d* of a liquid, of which as little as 5 mg. can be used and identified. The method consists of fractionating the sample by pumping through a series of appropriately cooled traps into the apparatus where the *d* and v.p. of the liquid are measured in a micropyknometer and manometer. Procedure is detailed and results on *cyclo*pentane, Δ^{α}- and Δ^{β}-pentene are presented. J. D. R.

Wet combustion micro-method for determination of carbon and hydrogen. Iodic acid as an oxidant for wet combustion.

B. E. Christensen and R. Wong (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 444—446).—The substance is oxidised with H_2SO_4–KIO_3 and the CO_2 evolved is determined by absorption in excess of $Ba(OH)_2$ followed by titration of excess of the base. The KIO_3 remaining after oxidation is determined by KI–$Na_2S_2O_3$, and the O consumed thus determined. From the wt. of CO_2 and the O consumed the C and H content of the sample is calc. Although numerous compounds are oxidised easily (1 hr. at 210°) by this method, others are incompletely oxidised after several hr. and the method is not generally applicable. Apparatus is described and procedures are detailed. J. D. R.

Semi-micro-method for determining of organic nitrogen. R. Belcher and A. L. Godbert (*J.S.C.I.*, 1941, **60**, 190—192).—20—50 mg. of the substance are digested for 45 min. with 4 ml. of conc. H_2SO_4 and 2 g. of a catalyst mixture (32 : 5 : 1) of K_2SO_4, $HgSO_4$, and Se. When necessary, reduction is first carried out with 5 ml. of HI and a trace of red P. The digestion mixture is distilled in 6 min. in a modified Pregl apparatus, and the NH_3 absorbed in 10 ml. of saturated aq. H_3BO_3, and titrated with 0·025N-HCl, using a mixed Me-red–methylene-blue indicator.

Determination of phosphorus in organic compounds on the semi-micro-scale. R. Belcher and A. L. Godbert (*Analyst*, 1941, **66**, 194).—The substance (20—50 mg.) is digested hot with 2 ml. of H_2SO_4 and successive 1-ml. portions of HNO_3 to destroy org. matter, the solution is cooled, diluted to 5 ml., heated to 90° with 1 ml. of 20% Na_2MoO_4 (just acidified with H_2SO_4) for every 1 mg. of P present, and the P is pptd. by addition of 3—5 ml. of 0·85% aq. $[Co(NH_3)_5NO_3](NO_3)_2$ [$= R(NO_3)_2$] over that required to colour the supernatant liquid pink. After cooling, the solution is filtered through a weighed Pregl filter-tube and the ppt. washed successively with 0·3N-HNO_3, H_2O, EtOH, and Et_2O, dried at 20° by drawing air through it for 5 min., and weighed as $RH_2PMo_{12}O_{41}$ containing 1·515% P. A. R. P.

Iodometric determination of peroxygen in organic compounds. V. R. Kokatnur and M. Jelling (*J. Amer. Chem. Soc.*, 1941, **63**, 1432—1433).—An iodometric method for the determination of peroxygen in org. compounds using $Pr^{\beta}OH$ (99%) as solvent is described. No blank titration is necessary and the method is of general applicability. W. R. A.

Characteristics of products of chemical and biochemical dissociation of ascorbic acid. II. Detection and determination of oxalic acid. E. A. Scheinkman (*Ukrain. Biochem. J.*, 1940, **16**, 111—121).—$H_2C_2O_4$ (I) can be detected in the dissociation of ascorbic (II) and dehydroascorbic acids (III) in an alkaline medium in the presence of H_2O_2 by the addition of $CaCl_2$ and microscopic observation of the crystals of CaC_2O_4. (I) is found at p_H 9—10 when dissociation takes place in the glycine buffer of Sörensen and with H_2O_2 at low p_H. In an alkaline medium using an oxidimetric method, 80—90% of the theoretical (according to Hirst *et al.*) (I) was determined whilst in H_2O_2 only 30—60% could be determined. In each case very little unchanged (II) or (III) remained. E. M. W.

Colorimetric determination of formaldehyde in presence of other aldehydes. W. J. Blaedel and F. E. Blacet (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 449—450).—The determination depends on the stability of the colour formed with Schiff's reagent and CH_2O, and the rapid fading of the colours produced with higher aldehydes. Direct colorimetric comparison is made between the sample and a sample of known and comparable concn. of CH_2O, and the colour allowed to fade for 2 hr. before the determination is made. Accuracy is 2—3%. J. D. R.

Determination of methylpentoses in presence of pentoses. B. H. Nicolet and L. A. Shinn (*J. Amer. Chem. Soc.*, 1941, **63**, 1456—1458).—Mixtures of methylpentoses (*A*) and many other sugars are determined by treatment with HIO_4 and determination of the MeCHO [from (*A*)] and HCO_2H (from sugars in general). R. S. C.

Identification and determination of pentose in nucleic acids and nucleoproteins. S. Gurin and D. B. Hood (*J. Biol. Chem.*, 1941, **139**, 775—785).—The carbazole test (A., 1940, III, 84) distinguishes xylose (I) from other pentoses and from methylpentoses, and yeast- from thymus-nucleic acid (II). It can be used for the determination of (I) in purine nucleotides and nucleosides, and of deoxyribose (III) in (II) and nucleoproteins. A preliminary bromination improves the vals. obtained for pentose (IV) in pyrimidine nucleotides, and has been used in the determination of (IV) in yeast-nucleic acid. The $NHPh_2$ reaction of Dische (A., 1930, 632) is more sp. for determining (III), of which (II) contains 40%. A. Li.

Micro-determination of lactose as lactobionic acid. S. M. Strepkov and N. K. Succhorukova (*Biochimia*, 1940, **5**, 140—143).—Lactose (in presence of monosaccharides) is oxidised by alkaline I solution to lactobionic acid, which is hydrolysed by aq. HCl; the resulting galactose is determined by the Hagedorn–Jensen procedure. F. O. H.

Determination of primary carbinol groups in carbohydrates. R. E. Reeves (*J. Amer. Chem. Soc.*, 1941, **63**, 1476—1477).—CH_2·OH in carbohydrates is determined by adding successively $NaHCO_3$–HIO_4, HCl–Na_3AsO_3, and NaOAc–dimedone (I). The neighbouring group must be such that (I) does not react with it. R. S. C.

Micro-titration of amino-acids and dipeptides in alcoholic solution by potassium hydroxide. L. M. Broude and K. I. Kokovichina (*Biochimia*, 1940, **5**, 217—224).—A modified Grassmann–Heyde technique is described (cf. Balson *et al.*, A., 1936, 91). F. O. H.

Determination of cystine : use of cuprous oxide for simultaneous reduction and precipitation of cystine as the cuprous mercaptide. C. A. Zittle and R. A. O'Dell (*J. Biol. Chem.*, 1941, **139**, 753—759; cf. Lucas *et al.*, A., 1941, III, 110).—Cystine is determined in protein hydrolysates by boiling the slightly acid solution with Cu_2O, and determining S gravimetrically or (better) cysteine colorimetrically (Sullivan reagent) in the ppt. Nucleic acid does not interfere. A. Li.

Determination of serine by periodate. B. H. Nicolet and L. A. Shinn (*J. Biol. Chem.*, 1941, **139**, 687—692).—CH_2O, formed by the action of IO_4', is determined as the dimedon derivative. Under the same conditions threonine yields MeCHO and can be determined simultaneously. In the absence of carbohydrates and hydroxylysine which also yield CH_2O, the vals. for serine are accurate to 2—3%. P. G. M.

Polarographic behaviour of histidine and other amino-acids.—See A., 1941, I, 379.

Salts of atropine, ephedrine, adrenaline, and procaine. F. M. Goyan and T. C. Daniels (*J. Amer. Pharm. Assoc.*, 1941, **30**, 98—105).—Potentiometric titration curves are given for the above bases with aspartic, glutamic, and lævulic acid and for atropine, ephedrine (I), and procaine with NaH_2PO_4 and of (I) with nicotinic acid. Hydrolytic changes appear to occur on evaporating the aq. salts of the bases to dryness. Physical properties of the salts are described. F. O. H.

Gravimetric determination of carbonyl groups in keto-steroids. H. B. Hughes (*J. Biol. Chem.*, 1941, **140**, 21—26).—CO groups are determined in small quantities of keto-steroids by treatment with Girard's reagent *T* (A., 1936, 1397) in AcOH–EtOH at 100° (bath), neutralising with NaOH to p_H 6·5—7·0, and pptn. with HgI and 10% AcOH. A. Li.

Polarographic determination of dehydro*iso*androsterone and other 3-hydroxy-Δ^5-steroids. E. B. Hershberg, J. K. Wolfe, and L. F. Fieser (*J. Biol. Chem.*, 1941, **140**, 215—232).—The micro-determination of 3-hydroxy-Δ^5-steroids by oxidation [$Al(OBu^{\nu})_3$ + $COMe_2$ in C_6H_6 at 100° (pressure)] and polarographic analysis of the Girard derivatives of the resulting 3-keto-Δ^4-steroids is described. $\alpha\beta$-Unsaturated keto-steroids must be determined separately before oxidation. The method is sp. for determining the amount of dehydro*iso*androsterone in the androgen fraction of urine and can be used for cholesterol. A. Li.

Colorimetric determination of 3-indolylacetic acid. J. Tanaka (*J. Pharm. Soc. Japan*, 1940, **60**, 19—23).—3-Indolylacetic acid (4—15 mg.-%), in absence of oxidising or reducing agents or excessive amounts of sugars, AcOH, HCO_2H, citric acid, $CO(NH_2)_2$, or KNO_3, is determined (±2%) by adding 2% $FeCl_3$ in 30% HCl, keeping at 37° for 4 hr., extracting by C_5H_{11}·OH the red colour produced, and determining the extinction coeff. at 530 mμ. Concn. of HCl and $FeCl_3$, temp., and time of reaction (<3 hr.) affect the result. R. S. C.

Bromo-complexes for identification of alkaloids.—See A., 1941, I, 387.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

NOVEMBER, 1941.

I.—ALIPHATIC.

Elimination reactions in organic chemistry. (A) **Mechanism.** M. L. Dhar, E. D. Hughes, C, K. Ingold, A. M. M. Mandour, F. R. Webb, and L. I. Woolf. (B) **Tautomerism and elimination.** E. D. Hughes (*Nature*, 1941, **147**, 812—813, 813—814).—(A) A summary of work reconciling and rationalising the Hofmann and Saytzeff rules. Reactions of "onium" salts proceeding by mechanism *E*2 (attack of a base on an alkyl proton) display "Hofmann influences" (=*H*); those going by mechanism *E*1 (prior formation of a carbonium ion) show "Saytzeff influences" (=*S*). Halide reactions by both mechanisms are governed by (*S*). Within the range investigated, these statements are true irrespective of whether the alkyl groups are primary, *sec.*, or *tert.*, provided they are saturated. Introduction of suitably placed unsaturation increases the field of application of (*S*). The responsible mechanism for (*H*) is undoubtedly the inductive effect, whilst that for (*S*) involves resonance due to the quasi-conjugation [cf. A., 1940, I, 390; identical with the "hyperconjugation" of Mulliken *et al.* (A., 1941, I, 100)] of the C_γ·H electrons with the electrons transferred in elimination from the dissolving C_β·H linking to the forming C_α:C_β linking. The greater is the no. of C_γ·H linkings the larger will be this effect; a much more powerful effect of the same kind arises when, in place of quasi-conjugation, full conjugation is produced by the provision of γ-unsaturation as in the $CH_2Ph·CH_2$· group. Independent electrostatic and resonance effects thus co-exist in elimination reactions, and being separately energised they may even work in opposition. Reactions involving the production of olefines from alcohols and ethers fall within the theoretical scheme outlined.

(B) The effect of alkyl groups on rate in the base-catalysed enolisation of ketones is of the Hofmann type. The base-catalysed equilibria of CAlkAlk':CH·CO_2H are essentially dependent on the same internal mechanism as (*S*) (above). H. B.

Production of hydrocarbons by catalytic conversion of carbon monoxide. Hydrogenation of carbon monoxide to produce hydrocarbons having more than one carbon atom in the molecule. Production of hydrocarbons by conversion of carbon monoxide with hydrogen. Catalytic conversion of carbon monoxide with hydrogen into hydrocarbons.—See B., 1941, II, 289, 290.

Production of saturated hydrocarbons.—See B., 1941, II, 290.

Production of saturated hydrocarbons with branched or more highly branched chains from saturated hydrocarbons with branched or less branched chains.—See B., 1941, II, 246.

Catalytic aromatisation and isomerisation of ββδ-trimethylpentane. S. J. Green and A. W. Nash (*Nature*, 1941, **148**, 53—54).—Considerable formation of mixed xylenes, and some $C_{10}H_8$, accompanied by cracking, occurs with pure $CH_2Pr^\beta Bu^\gamma$ at 550° with a liquid catalyst-space velocity of 0·33 c.c. per c.c. per hr. and a 6 at.-% Mo oxide-activated Al_2O_3 catalyst in a mild steel tube. L. S. T.

Determination of freezing points and amounts of impurity in hydrocarbons from freezing and melting curves. B. J. Mair, A. R. Glasgow, jun., and F. D. Rossini (*J. Res. Nat. Bur. Stand.*, 1941, **26**, 591—620).—Time–temp. freezing and melting curves are analysed and a procedure for determining the f.p. of a substance and the amount of impurity in it is developed to apply to cases in which a known portion of the curves represents thermodynamic equilibrium between liquid and cryst. phases. The method is shown to be applicable to hydrocarbons containing 0·6—11·5 mol.-% of solute. J. W. S.

Polymerisation of ethylene.—See B., 1941, II, 290.

Biochemical synthesis of carbon chains of isoprene type.—See A., 1941, III, 937.

Synthesis of hydrocarbons with conjugated ethylenic linkings. III. V. I. Esafov, V. M. Guliakov, V. V. Kargopoltzeva, A. P. Kulakova, G. V. Razmislov, and N. D. Toporov (*J. Gen. Chem. Russ.*, 1940, **10**, 1973—1977).—COMeEt and CaC_2 (7 hr. at 100°) yield *γ-methyl-Δγ-hepten-ε-one* (I), b.p. 164—165°. With MgEtBr in Et_2O this gives *γ-methyl-ε-ethyl-Δγε-heptadiene*, b.p. 154°, and with *iso*-C_5H_{11}·MgBr a mixture, b.p. 194—200°, of *γ-methyl-ε-isoamyl-Δγε-heptadiene* and *βζ-dimethyl-ε-ethyl-Δδζ-nonadiene*. The Grignard reaction did not take place as above in the cases of CH_2Ph·MgBr and (I) or mesityl oxide. R. T.

Manufacture of butadiene, chlorobutene, and trichlorobutane.—See B., 1941, II, 290.

Production of acetylene, acetone, and methyl acetate.—See B., 1941, II, 245.

Isomerisation of chloroalkanes.—See B., 1941, II, 247.

Production of alkyl halides from alkenes and hydrogen halide.—See B., 1941, II, 247.

Manufacture of alkyl chlorides.—See B., 1941, II, 291.

Manufacture of chloroform.—See B., 1941, II, 291.

Manufacture of nitromethane.—See B., 1941, II, 247.

Production of alcohols by catalytic hydrogenation of esters of carboxylic acids.—See B., 1941, II, 248.

Addition of βγ-unsaturated alcohols to the active methylene group. III. Scope and mechanism of the reaction. M. F. Carroll (*J.C.S.*, 1941, 507—511; cf. A., 1940, II, 266, 347).—At 150—250° in the presence of an alkaline catalyst (NaOAc, NaOEt, KOH) βγ-unsaturated alcohols with a compound containing an active CH_2 [$CH_2Ac·CO_2Et$, $CHBuAc·CO_2Et$, or $CH_2(CO_2Et)_2$] give normal additive products; from an alcohol ROH, the substances obtained are EtOH, CO_2, ROAc, $COMe_2$, CH_2AcR (or R' where rearrangement occurs) and the olefine from ROH. With $CH_2Ac·CO_2Et$ and saturated alcohols, the ester is obtained. The reactivity of the groups attached to the active CH_2 is in the order: $CH_2(CO_2R)_2$ > R·CO·CH_2·CO_2R' > R·CO·CHR'·CO_2R'' > R·CO·CH_2·COR'. The mechanism of the reactions is discussed, and the results are applied to explain some analogous reactions. F. R. S.

Search for a stable substituted vinyl alcohol. F. H. Stodola (*Science*, 1941, **93**, 452).—Alternative formulæ for the "substituted vinyl alcohol" and the corresponding ketone prepared by Fuson *et al.* (A., 1941, II, 222) are suggested. The behaviour of the alcohol on oxidation (CrO_3 in AcOH) is difficult to reconcile with the vinyl alcohol formula, without assuming an unprecedented αδ dehydrogenation. L. S. T.

Synthesis of primary βγ-unsaturated alcohols, glycols, and their derivatives. S. N. Chitrik (*J. Gen. Chem. Russ.*, 1940, **10**, 2098—2100).—The sole product of reaction of Mg with $(CH_2Br·CH:)_2$ in Et_2O is butadiene. *p*-$C_6H_4Me·SO_3·CH_2·CH_2Cl$ does not react with CHPh:CH·MgBr in Et_2O, R. T.

Purification of glycerol by crystallisation.—See B., 1941, II, 245.

Production of pentaerythritol.—See B., 1941, II, 248.

Manufacture of ethers from olefines.—See B., 1941, II, 248.

Effect of alkalinity or acidity on stability of ether.—See B., 1941, II, 245.

Action of oxides of nitrogen on unsaturated ethers. I. Action of nitrous anhydride on methyl allyl ether. N. J. Maslov (*J. Gen. Chem. Russ.*, 1940, **10**, 1915—1917).—$OMe{\cdot}CH_2{\cdot}CH{:}CH_2$ in Et_2O when saturated at −10° with N_2O_3 yields *Me γ(β)-nitro-β(γ)-nitrosopropyl ether*, m.p. 106—107°, reduced by $SnCl_2$ in HCl to $OMe{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2$ [*dihydrochloride*, m.p. 214° (*platinichloride*); *dipicrate*, m.p. 210°]. R. T.

Acetone-[*iso*propylidene-]glyceraldehyde and optically active glycerides. IX. Configuration of natural batyl, chimyl, and selachyl alcohols. E. Baer and H. O. L. Fischer (*J. Biol. Chem.*, 1941, **140**, 397—410).—*l*(−)-*iso*Propylideneglycerol in $(CH_2{\cdot}OMe)_2$ is added to a cold solution of Na–$C_{10}H_8$ in the same solvent. When the green colour has disappeared, *n*-$C_{18}H_{37}I$ is added and the solution is boiled for 48 hr. After removal of solvent and dihydronaphthalene at 160°/10—15 mm., d-iso*propylidene-α*-n-*octadecylglycerol* (**I**), m.p. 34—36°, $[\alpha]_D^{40}$ −12·6°, is isolated by distillation in a mol. still. l- (**II**), m.p. 32·5—33·5°, $[\alpha]_D^{40}$ +12·4°, and dl- (**III**), m.p. 32—33°, -iso*propylidene-α*-n-*octadecylglycerol* are obtained similarly. (**I**) is hydrolysed by 80% AcOH at 80° to d-α-n-*octadecylglycerol* (**IV**), m.p. 71—72°, $[\alpha]_D$ +0·8°, +0·7°, and +4·0° in $CHCl_3$ (*c* = 84, 3·83, and 1·0, respectively), identical with natural batyl alcohol, (**V**). (**II**) and (**III**) similarly afford l- (**VI**), m.p. 71—72°, $[\alpha]_D$ 0·0°, −1·6°, and −2·3° in $CHCl_3$ (*c* = 9·98, 3·17, and 1·10, respectively), and dl- (**VII**), m.p. 71—71·5°, -α-n-*octadecylglycerol*. (**IV**) gives an α′β-diacetate, readily interconvertible polymorphic forms, m.p. 34—34·5° and 42—43° respectively, $[\alpha]_D$ −7·6° in $CHCl_3$ free from EtOH, an α′β-diphenylurethane, m.p. 100·5—101·5°, $[\alpha]_D$ −6·4° in C_5H_5N, and an α′β-*di*-p-*nitrobenzoate*, m.p. 65·5—66·5°, $[\alpha]_D$ −27·9° in dry $CHCl_3$; the first two compounds are identical with those derived from (**V**). Similarly (**VI**) gives an α′β-*diacetate*, varieties, m.p. 34—34·5° and 42—43°, respectively, $[\alpha]_D$ +7·6°, $[\alpha]_{5461}$ +8·6° in $CHCl_3$ free from EtOH, an α′β-*diphenylurethane*, m.p. 101—101·5°, $[\alpha]_D$ +6·5° in dry C_5H_5N, and an α′β-*di*-p-*nitrobenzoate*, m.p. 66·5—67°, $[\alpha]_D$ +29·1° in CCl_4. The α′β-*diacetate*, b.p. 180—183°/10^{-3} mm., m.p. 34—34·5°, α′β-*diphenylurethane*, m.p. 94·5—95°, and α′β-*di*-p-*nitrobenzoate*, m.p. 73·5—74°, of (**VII**) are described. The appropriate *iso*propylideneglycerol is transformed by *n*-$C_{16}H_{33}I$ into d- (**VIII**), $[\alpha]_D^{22}$ −11·9°, l- (**IX**), $[\alpha]_D$ +12·1°, and dl- (**X**) -iso*propylidene-α*-n-*hexadecylglycerol*. Hydrolysis of (**VIII**) gives d-α-n-*hexadecylglycerol*, m.p. 62·5—63·5°, $[\alpha]_D^{25}$ +3·0° in dry $CHCl_3$ (α′β-*diphenylurethane*, m.p. 97·5—98°, $[\alpha]_D$ −6·9° in dry C_5H_5N; α′β-*di*-p-*nitrobenzoate*, m.p. 52°, $[\alpha]_D$ −29·2° in dry $C_2H_2Cl_4$), identical with natural chimyl alcohol (**XI**). Similarly (**IX**) gives l-α-n-*hexadecylglycerol*, m.p. 63—64°, $[\alpha]_D^{22}$ ±0·0° (*c* = 10·1), $[\alpha]_D^{25}$ −1·3° (*c* = 3·22) and −2·2° (*c* = 1·13) in dry $CHCl_3$ (α′β-*diphenylurethane*, m.p. 97—98°, $[\alpha]_D$ +7·17° in dry C_5H_5N; α′β-*di*-p-*nitrobenzoate*, m.p. 52—53°, $[\alpha]_D$ +29·7° in dry $C_2H_2Cl_4$), and (**X**) affords dl-α-n-*hexadecylglycerol*, m.p. 62—63° (α′β-*diphenylurethane*, m.p. 92°; α′β-*di*-p-*nitrobenzoate*, m.p. 52—53°). (**V**) and (**XI**) therefore belong to the *d* series to which also selachyl alcohol can be assigned on account of its close relationship to (**V**).

The unsaponifiable matter from ratfish (*Chimaera monstrosa*) liver oil consists mainly of (**XI**) with a small proportion of (**V**). H. W.

Chemical warfare materials. XXIV. Determination of "yellow cross" [ββ′-dichlorodiethyl sulphide] by the spectrophotometric method. H. Mohler (*Helv. Chim. Acta*, 1941, **24**, 571—573).—$(Cl{\cdot}[CH_2]_2)_2S$ may be determined spectrophotometrically in hexane using the band 202—203 mμ. A concn. >0·00003M. is necessary. Beer's law holds over the range 0·0003—0·0015M. F. J. G.

[Velocity of] hydrolysis of ββ′-dichlorodiethyl sulphide.—See A., 1941, I, 420.

Manufacture of organic anhydrides.—See B., 1941, II, 249.

Preparation of alkyl formates.—See B., 1941, II, 249.

Azeotropic distillation for dehydrating acetic acid.—See B., 1941, II, 289.

Configurational relationship of α-methylheptoic and γ-methylnonoic acids. P. A. Levene and M. Kuna (*J. Biol. Chem.*, 1941, **140**, 255—257).—α-Methylheptoic acid, $[\alpha]_D^{25}$ +8·48°, resolved by cinchonidine, by the usual reactions yields the Et ester, $[\alpha]_D^{25}$ +8·91°, β-methylheptan-α-ol, $[\alpha]_D^{25}$ −4·01°, and α-iodo-β-methylheptane, $[\alpha]_D^{25}$ +1·05°, which with $CH_2(CO_2Et)_2$ and NaOEt yields γ-methylnonoic acid, b.p. 92°/0·1 mm., $[\alpha]_D^{25}$ +0·46° (cf. A., 1932, 360). All [α] are homogeneous. A. Li.

Polymorphism of unsaturated fatty acids C_{18}. G. Ravitsch, V. Volnova, and T. Kuzmina (*Acta Physicochim. U.R.S.S.*, 1941, **14**, 403—413).—The polymorphism of oleic acid (**I**) has been studied by means of photomicrography and of heating and cooling curves. Apparatus for determining cooling curves with very slow cooling is described. When (**I**) is very slowly cooled the break on the cooling curve usually observed at ~9° is resolved into two, at 11° and at 8·5°; this is attributed to contamination with saturated fatty acids. The heating curves show additional thermal effects at 20—21°, the position depending on the previous history of the sample. These indicate the existence of a new modification of (**I**), m.p. 20—20·5°, and this is confirmed by photomicrographs. F. J. G.

Alkenyl esters of unsaturated monocarboxylic acids of the $C_nH_{2n-1}{\cdot}CO_2H$ series. A. D. Petrov and V. D. Azatian (*J. Appl. Chem. Russ.*, 1940, **13**, 1602—1605).—Oleic, undecenoic, acrylic, and crotonic acid and Δ$^{\alpha}$-hexinene at 50—70° in presence of HgO and BF_3,Et_2O give COMeBu, but not the expected esters. At >30° and in Et_2O, β-Δ$^{\alpha}$-, b.p. 110°/30 mm., and β-Δ$^{\gamma}$-*hexenyl*, b.p. 89·5—92·5°/18 mm., and β-Δ$^{\alpha}$-*pentenyl crotonate*, b.p. 95°/30 mm., are obtained from Δ$^{\alpha}$- and Δ$^{\gamma}$-hexinene and Δ$^{\alpha}$-pentinene, respectively. R. T.

Separation and identification of fatty acids. III. Preparation of pure oleic and elaidic acid by the hydroxamic acid method. Y. Inouye and H. Yukawa (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 411—413; cf. A., 1940, II, 336).—*Oleohydroxamic acid*, m.p. 61°, obtained from olive oil by treatment with NH_2OH,HCl and NaOEt, is quantitatively converted into oleic acid by hydrolysis with boiling EtOH–dil. H_2SO_4. *Elaidohydroxamic acid*, m.p. 91°, prepared similarly, yields elaidic acid when hydrolysed under the same conditions. J. N. A.

Constitution of spiculisporic acid, a metabolic product of the mold fungus *Penicillium spiculisporum* (Lehman). M. Asano and Y. Kameda [with, in part, T. Naruse] (*J. Pharm. Soc. Japan*, 1941, **61**, 57—63).—Spiculisporic acid (**I**) is the lactone of γ-hydroxy-γδ-dicarboxypentadecoic acid, and not of the βδ-dicarboxy-acid as stated by Clutterbuck *et al.* (A., 1931, 1092). (**I**) affords γ-ketopentadecoic acid (**II**) (semicarbazone, m.p. 124—125°), identical with that obtained by condensing $Me{\cdot}[CH_2]_{10}{\cdot}CO{\cdot}CHNa{\cdot}CO_2Et$ and $CH_2Br{\cdot}CO_2Et$ at 100° for 7 hr., followed by HI (*d* 1·7) at 100° (bath). $CO(CH_2{\cdot}CO_2Et)_2$–NaOEt–$CH_2Br{\cdot}CO_2Et$ at 110° yield a substance, converted by *n*-$C_{10}H_{21}I$–NaOEt at 120° into a product reduced by Na–Hg to laurone, $CO(C_{11}H_{23}\text{-}n)_2$, and (**II**). (**I**) and red P–HI (*d* 1·7) at 190—210°, followed by Zn–AcOH, and then KOH–EtOH at 100° (bath), afford para-*tetradecane-αγδ-tricarboxylic acid* (**III**), m.p. 160—162° (*tri*-p-*phenylphenacyl* ester, m.p. 108—111°), and the meso-*αγδ-tricarboxylic acid* (**IV**), m.p. 109—111°. $CH_2(CO_2Et)_2$, $Cl{\cdot}[CH_2]_2{\cdot}CO_2Et$, and NaOEt afford $CH(CO_2Et)_2{\cdot}[CH_2]_2{\cdot}CO_2Et$, b.p. 126—128°/2 mm., converted into the Na derivative and then condensed with *n*-$C_{10}H_{21}{\cdot}CHBr{\cdot}CO_2Et$ at 120—130° to *Et$_4$ tetradecane-αγγδ-tetracarboxylate*, b.p. 210—225°/2 mm., which on hydrolysis by 50% KOH–EtOH at 100° (bath) and then heating at 140—150° yields (**III**) and (**IV**). *n*-$C_{10}H_{21}{\cdot}CNa(CO_2Et)_2$, $CH_2Br{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CO_2Et$, and NaOEt at 140—150° afford *Et$_4$ tetradecane-βγδδ-tetracarboxylate*, b.p. 215—217°/1 mm., converted by hydrolysis (KOH–EtOH) and then decarboxylation (at 150—155°) into *tetradecane-αβδ-tricarboxylic acid* (**V**), m.p. 145—147°; if (**I**) possessed the constitution attributed by Clutterbuck *et al.* (*loc. cit.*), it should yield (**V**). A. T. P.

α-Hydroxy-α-methylthiodiacetic acid. E. Larsson (*Svensk Kem. Tidskr.*, 1941, **53**, 1—5).—$CO_2H{\cdot}CH_2{\cdot}S{\cdot}CMe(OH){\cdot}CO_2H$ (**I**) [from $SH{\cdot}CH_2{\cdot}CO_2H$ (**II**) and $AcCO_2H$] is completely dissociated into its components in alkaline solution. In 0·1N-HCl k = 0·015 and in H_2O k = 0·01—0·03. The formation and dissociation of (**I**) are both very rapid. Similar compounds are formed from (**II**) and $CHO{\cdot}CO_2H$ (*k* very small in acid solution and dissociation slow) and CH_2O (k = 0·3 in H_2O and dissociation rapid), but not $COMe_2$. M. H. M. A.

Basic catalysis of transformation and decomposition of monosaccharides. II. Epimerisation of arabinose by anions of weak acids in acid media. A. D. Braun and R. K. Konnova (*Biochimia*, 1940, **5**, 497—501).—Anions of weak acids cause epimerisation of arabinose in acid medium. Ketopentose, which is readily decomposed by acid, is thus produced from aldopentose by OAc′ ions, the resulting solution being almost free from aldopentose. $NHPh{\cdot}NH_2$ in presence of HSO_3' is used, *e.g.*, in urine analysis, to detect ketopentose in presence of aldoses and other aldehydes. W. McC.

Studies of the chemical properties of carbohydrates by means of heavy oxygen. I. Exchange reactions of oxygen between monoses and water. K. Goto and T. Titani (*Bull. Chem. Soc. Japan*, 1941, **16**, 172—177).—In H_2O containing an excess of ^{18}O at 100°, glucose, fructose, galactose, xylose, and arabinose exchange 1 O. In presence of acid or base >1 O is gradually exchanged although decomp. also occurs. R. S. C.

Active form of simple sugars. VII. Reactivity of fructose 1 : 6-diphosphate. A. V. Stepanov and B. N. Stepanenko (*Biochimia*, 1940, **5**, 567—573).—The proportions of HCN bound by fructose 1 : 1-diphosphate (I), fructose 1-monophosphate, and fructose during 2 hr. are 30, 13, and 0%, respectively. The high val. for (I) shows that much of this compound in the equilibrium mixture is in the keto-form. Phosphorylation of hexoses is accompanied by conversion from a cyclic form into an open-chain, more reactive keto-form. This conversion occurs gradually during the first stages of glycolysis, the six-C chain, which is most stable in free glucose, being finally disrupted. W. McC.

Enzymic hydrolysis of disaccharides and halogenosalicins. W. W. Pigman (*J. Res. Nat. Bur. Stand.*, 1941, **27**, 1—8; cf. A., 1939, III, 99).—Enzymes of almond emulsin hydrolyse all of the disaccharides with β-glucosidic linkings so far tried, in agreement with the Weidenhagen theory. Rates of hydrolysis for gentiobiose (6-β-glucosido-*d*-glucose), 4-β-glucosido-*d*-mannose (I), and lactositol (4-β-glucosido-*d*-sorbitol) are compared with those of other disaccharides. Small changes in structure of the aglucone sugar have a large effect on rate of enzymic hydrolysis; *e.g.*, although (I) differs from cellobiose in the configuration of only one C atom, a very marked decrease is observed in the case of (I). Theoretical considerations are discussed, and mechanisms of reaction are suggested. Rates of enzymic fission for *p*-chloro-, -bromo-, and -iodo-salicins are similar, but the relative ease of fission is I- > Br- > Cl-derivative; introduction of halogen in the *p*-position of the salicin aglucone reduces the rate to <¼ of the val. for salicin. A. T. P.

Hydrolysis of laminarin. Isolation of a new glucose disaccharide. V. C. Barry (*Sci. Proc. Roy. Dublin Soc.*, 1941, **22**, 423—429; cf. A., 1939, III, 409).—*Laminaribiose* (? glucose-3-β-glucoside), m.p. >90° (decomp.) (one specimen was cryst., m.p. 161—162°), $[\alpha]_D^{15}$ +20·8° (25 min.) in H_2O, +16·14° (21 hr.) (*osazone*, m.p. 195°, $[\alpha]_D^{19}$ −79·6° in EtOH; cf. Zechmeister *et al.*, A., 1934, 810), is present in the products of partial hydrolysis (N-$H_2C_2O_4$ or snail-juice) of laminarin (I). It is hydrolysed by emulsin to glucose. The constitution of (I) is discussed. A. Li.

Carbohydrate group of egg proteins. III. P. A. Levene (*J. Biol. Chem.*, 1941, **140**, 279—284).—The polysaccharide (I) from egg proteins (A., 1929, 1478) could not be satisfactorily methylated, but on hydrolysis (10N-HCl at room temp.) yields d-*mannoglucosaminide*, which when hydrolysed gives mannose and when reduced (Raney Ni at 75° under pressure) yields *mannitolchondrosaminide*, acetylated and hydrolysed (boiling 20% HCl) to glucosamine, but no mannose. (I) with 5% HNO_3 at 100° under pressure, then conc. HNO_3 at room temp., yields no mucic acid. A. Li.

Optical rotatory relationships exhibited by aromatic and aliphatic glucosides. W. W. Pigman and H. S. Isbell (*J. Res. Nat. Bur. Stand.*, 1941, **27**, 9—25).—A comparison of rotations of numerous glucosides shows that aromatic groups (Ph and substituted Ph) produce rotational effects different from those produced by aliphatic radicals. When an aromatic nucleus is attached to an asymmetric C through an O linking, the rotatory contributions of other asymmetric C attached to the former C are greater by a fairly const. amount than when the attached group is aliphatic. Substituted phenyl-β-glucosides are much more lævorotatory than the aliphatic β-glucosides. Phenyl-β-glucosides when substituted by *o*-*p*-directing groups in any position, or *m*-directing groups in the *o*-position, have vals. of $[M]_D^{20}$ (in H_2O) of ~−17,000 to −20,000, whereas those of aliphatic β-*d*-glucosides are ~−6500 to −9500, except in the case of glucosides of *tert.* alcohols (~−4000); *m*-directing groups in *m*- or *p*-positions, however, cause an increase in val. and *p*-nitrophenyl-β-glucoside has a val. of $[M]_D^{20}$ −31,130. A marked decrease in val. is caused by substituting two groups in the *o*-positions of phenyl-β-glucoside, *e.g.*, the *o*-*o*′-xylenyl derivative has a val. of −4380 (cf. *o*-*p*-isomeride, −18,480). In a series of related glucosides, aliphatic or aromatic, the mol. rotations of the β-glucosides ∝ rotatory contributions of the glucosidic carbons. Vals. of $[M]_D$ and $[\alpha]_D$ for many α- and β-glucosides are recorded, with relevant literature. A parallelism observed between the dissociation consts. of phenols and the optical properties of the corresponding substituted phenyl-β-glucosides supports the view that the optical rotation is conditioned by the same intramol. electronic forces as those which control dissociation of phenolic H. β-*d*-α-Mannoheptose hexa-acetate (improved prep.), PhOH, and *p*-$C_6H_4Me{\cdot}SO_3H$ or $ZnCl_2$ at 100° (bath) give the acetylated glycoside, converted by MeOH–$Ba(OMe)_2$ into the *phenyl*-d-α-*mannoheptosides*, α-, m.p. 212°, $[\alpha]_D^{20}$ +207° in H_2O, and (more sol.) β-form, m.p. 189—190°, $[\alpha]_D^{20}$ −39·8° in H_2O. *Phenyl*-α-d-*taloside tetra-acetate*, m.p. 103·5—104°, $[\alpha]_D^{20}$ +97·4° in $CHCl_3$, affords *phenyl*-d-*taloside*, m.p. 165·5—166·5°, $[\alpha]_D^{20}$ +138° in H_2O. β-*d*-α-Glucoheptose hexa-acetate, PhOH, and $ZnCl_2$ give *phenyl*-d-α-*glucoheptoside penta-acetate*, α-, m.p. 154—155°, $[\alpha]_D^{20}$ +167° in $CHCl_3$, and β-form, m.p. 97°, $[\alpha]_D^{20}$ +8·0° in $CHCl_3$, deacetylated to *phenyl*-α-, m.p. 191—192°, $[\alpha]_D^{20}$ +163° in H_2O, and -β-d-α-*glucoheptoside*, m.p. 167—168°, $[\alpha]_D^{20}$ −89·7° in H_2O, respectively. A. T. P.

Constitution of butrin. P. S. Rao (*Current Sci.*, 1940, **9**, 492; cf. A., 1937, II, 445).—Butrin (I) and CH_2N_2 yield a *Me*$_4$ *ether*, hydrolysed to a monomethylbutein. Hence (I) is not a bioside but a diglucoside of butin with the sugar nuclei in different positions. E. M. W.

Syntheses of 2 : 4-dimethyl-β-methylglucoside. M. H. Adams, R. E. Reeves, and W. F. Goebel (*J. Biol. Chem.*, 1941, **140**, 653—661).—β-Methylglucoside 2 : 4 : 6-triacetate 3-*p*-toluenesulphonate is de-acetylated [$Ba(OMe)_2$ in dry MeOH at 0°] to the non-cryst. *β-methylglucoside* 3-p-*toluenesulphonate*, transformed by CPh_3Cl in C_5H_5N at 100° into the amorphous 6-*triphenylmethyl-β-methylglucoside* 3-p-*toluenesulphonate* (I), m.p. 76—78°, $[\alpha]_D^{22}$ −22·0° in $CHCl_3$ (2 : 4-*diacetate*, m.p. 145—147°, $[\alpha]_D^{25}$ +14·5° in $CHCl_3$). Repeated methylation of (I) by Ag_2O and MeI gives 6-*triphenylmethyl*-2 : 4-*dimethyl-β-methylglucoside* 3-p-*toluenesulphonate*, $[\alpha]_D^{25}$ −1·05° in $CHCl_3$, converted by HBr–AcOH into 2 : 4-*dimethyl-β-methylglucoside* 3-p-*toluenesulphonate*, $[\alpha]_D^{26}$ −2·3° in $CHCl_3$, and thence by Na–Hg in MeOH into 2 : 4-*dimethyl-β-methylglucoside* (II), dimorphous, m.p. 105—106° or 122—124°, $[\alpha]_D^{25}$ −18·6° in $COMe_2$, in very poor yield. Di*iso*propylideneglucose *p*-toluenesulphonate is converted by boiling 2% HCl–MeOH into a mixture of α- and β-methylglucoside 3-*p*-toluenesulphonates from which, after successive treatments with CPh_3Cl and Ac_2O–C_5H_5N, 6-*triphenylmethyl-α-methylglucoside* 2 : 4-*diacetate* 3-p-*toluenesulphonate*, m.p. 191—192°, $[\alpha]_D^{25}$ +72·8° in $CHCl_3$, is isolated. Gradual addition of solid KOH to di*iso*propylideneglucose dissolved in CH_2PhCl at 100° affords 3-benzyldi*iso*propylideneglucose, hydrolysed by dil. HCl to 3-benzylglucose, m.p. 138—141°, $[\alpha]_D$ +20·3° to +41·9° in H_2O (equilibrium) (lit. m.p. 127—128°, $[\alpha]_D$ +29·1°), which gives the non-cryst. 3-*benzyl*-6-*triphenylmethylglucose* (III), $[\alpha]_D^{25}$ +19·4° (equilibrium) in $CHCl_3$ [1 : 2 : 4-*triacetate*, m.p. 150—205° (mixture of α- and β-forms)]. (III) is methylated (MeI + Ag_2O) with great difficulty and the product of the reaction is converted by HBr–AcOH followed by Na and 95% EtOH into (II) in small yield. 2 : 4-Dimethyl-α-methylglucoside (IV) has m.p. 79—80°. (II) and (IV) are transformed by $NHPh{\cdot}NH_2$ into 4-methylglucosazone, thus establishing the presence of OMe at $C_{(2)}$. H. W.

Synthesis of glucosides. K. Nisizawa (*Bull. Chem. Soc. Japan*, 1941, **16**, 155—160).—β-*d*-Galactose penta-acetate (I), guaiacol (II), and *p*-$C_6H_4Me{\cdot}SO_3H$ (III) at 125—128° give a mixture, converted by boiling 0·2N-NaOMe–MeOH into β-*guaiacyl*-d-*galactoside* (IV), m.p. 203—204°, $[\alpha]_D^{20}$ −44·64° in H_2O, and a residue, which with Ac_2O–C_5H_5N at 100° gives

α-guaiacyl-d-*galactoside tetra-acetate* (V), m.p. 82—84°, $[\alpha]_D^{22}$ +227·6° in $CHCl_3$, and thence *α-guaiacyl*-d-*galactoside*, m.p. 140—142°, $[\alpha]_D^{21}$ +211·4° in H_2O. (IV), $[\alpha]_D^{28}$ −44·48° in H_2O, is better obtained by way of its *tetra-acetate*, m.p. 100—102°, $[\alpha]_D^{22}$ −16·71° in $CHCl_3$, from acetobromogalactose (VI), (II), NaOH, and a little H_2O in $COMe_2$ at room temp. At 100° (I), (II), and $ZnCl_2$ give mainly (V), but at 125° the same mixture is obtained as with (III). At 120°, (I), *m*-cresol, and $ZnCl_2$ give α-m-*tolyl*-d-*galactoside* (VII), m.p. 150—152°, $[\alpha]_D^{19}$ +207·0° in H_2O, by way of its *tetra-acetate*, m.p. 75—76°, $[\alpha]_D^{17}$ +178·0° in $CHCl_3$; at 125—128° with $ZnCl_2$ or (III) (cf. Helferich *et al.*, A., 1935, 201), mixed crystals (? a 1 : 1 additive *compound*), m.p. 175—178°, $[\alpha]_D^{13}$ +81·0° in H_2O, of (VII) and its β-analogue (m.p. 166—167°, $[\alpha]_D$ −44·3° in H_2O) are obtained. *p*-OH·C_6H_4·COMe and (VI) give (as above) *β*-p-*acetylphenyl*-d-*galactoside tetra-acetate* (52%), m.p. 146—147°, $[\alpha]_D^{28}$ −51·69° in C_6H_6, but (I) in presence of $ZnCl_2$ or (III) at 127—128° gives only the *α-galactoside*, m.p. 158—160°, $[\alpha]_D^{29}$ +226·2° in H_2O, by way of the *tetra-acetate*, m.p. 155—157°, $[\alpha]^{23\text{ or }29}$ +29·0° in $CHCl_3$. *o*-OH·C_6H_4·CHO, (VI), and Ag_2O in quinoline give *β*-o-*aldehydophenyl*-d-*galactoside*, m.p. 237—239°, $[\alpha]_D^{30}$ −23·6° in H_2O, by way of the *tetra-acetate* (21·6%), m.p. 107—109°, $[\alpha]_D^{23}$ −13·74° in $CHCl_3$. *s-m*-Xylenol, (VI), and NaOH in $COMe_2$ give *β*-s-m-*xylyl*-d-*galactoside*, m.p. 193—194°, $[\alpha]_D^{22}$ −43·0° in H_2O, by way of the *tetra-acetate* (24·6%), m.p. 116—117°, $[\alpha]_D^{23}$ −19·0° in C_6H_6; *β*-p-*allylphenyl*-d-*galactoside*, m.p. 196—198°, $[\alpha]_D^{20}$ −59·6° in N-NaOH (*tetra-acetate*, m.p. 140—141°, $[\alpha]_D^{23}$ −52·5° in C_6H_6), is similarly obtained. The procedure using (I) and $ZnCl_2$ at 127—128° or 130—132° yields *α-phenyl-*, $+H_2O$, m.p. 88—90°, $[\alpha]_D^{17}$ +199·2° in H_2O (*tetra-acetate*, m.p. 131—132°, $[\alpha]_D$ +175·5° in $CHCl_3$), *α*-p-*tolyl-*, m.p. 190—191°, $[\alpha]_D^{18}$ +178·0° in H_2O (*tetra-acetate*, $[\alpha]_D^{25}$ +162·0° in $CHCl_3$), and *α*-o-*anisyl*-*β*-*galactoside*, $+H_2O$, m.p. 150—153°, $[\alpha]_D^{18}$ +156·4° (amorphous tetra-acetate, $[\alpha]_D^{15}$ +170·5° in $CHCl_3$). BuOH, (VI), and Ag_2CO_3 at 60° give *β-butyl*-d-*galactoside*, m.p. 99—100°, $[\alpha]_D^{15}$ −8·4° in H_2O, by way of the *tetra-acetate*, m.p. 60—62°, $[\alpha]_D^{20}$ −13·8° in $CHCl_3$. R. S. C.

Constituents of the Chinese drug " chih-shih " (*Citrus fusca*, **Lour., of the family Rutaceæ) ; derivatives of hesperitin.** L. C. Waung (*J. Pharm. Soc. Japan*, 1940, **60**, 164—168).—Extraction of the fruits of *C. fusca*, Lour., with warm EtOH gives 6—7% of material, $C_{28}H_{34}O_{15}$, m.p. 236—237°, identical with the new hesperidin (I) of Kolle and Gloppe (A., 1936, 970). Hydrolysis (2% HCl or H_2SO_4) of (I) gives hesperitin (II), m.p. 224—226° (oxime, m.p. 230—231°). (II) is transformed by cold Ac_2O containing a trace of conc. H_2SO_4 into the monoacetate, m.p. 127°, which does not give a colour with $FeCl_3$ but becomes cherry-red under the influence of Mg + HCl, by Ac_2O at 100° into the *diacetate*, m.p. 127—129°, which gives a red colour with Mg + HCl and a dark violet colour with $FeCl_3$, and by NaOAc and boiling Ac_2O into a *tri-*, m.p. 165—167° (which is not coloured by Mg + HCl or by $FeCl_3$), and a *tetra-acetate*, m.p. 104—106°, which gives no colour with $FeCl_3$ but a positive reaction with Mg + HCl. The product of the action of an excess of CH_2N_2 on (II) in Et_2O is separated by MeOH into Me_2 esters, m.p. 133—136° (III) and 153—155° (IV) respectively, and a Me_1 ester, m.p. 161—163°, all of which give positive reactions with $FeCl_3$ and with Mg + HCl. (III) and (IV) are transformed by Ac_2O and concn. H_2SO_4 into the *monoacetate*, m.p. 153—154·5°. Glucose and rhamnose are obtained by hydrolysis of (I). H. W.

Glycerolysis of starch. Mol. wt. and viscosity of the products. Y. Tsuzuki (*Bull. Chem. Soc. Japan*, 1941, **16**, 161—170).—Increasing the duration or temp. (180—200°) of heating potato, wheat, or rice starch in glycerol causes greater decrease in α and $\eta_{sp.}$ of the product and its acetate and greater increase in (*a*) the glycerol content of the product and its acetate and (*b*) the Ac content of the acetate. The mol. wt. calc. from the glycerol content (end-group) agrees approx. with that determined by cryoscopy in $(CH_2Br)_2$. The equation, $\eta_{sp.}/c = K_m M + k$ (k = const.), gives K_m independent of chain length (cf. Meyer *et al.*, A., 1935, 1318). Wheat starch degrades more easily than does rice starch. R. S. C.

Hydrolysis and catalytic oxidation of cellulosic materials. R. F. Nickerson (*Ind. Eng. Chem.*, 1941, **33**, 1022—1026; cf. B., 1941, II, 111).—Curves relating time (t) and CO_2 evolved (C) are recorded for the hydrolysis of celluloses (I) of various origins and their derivatives by boiling HCl (2·4) + $FeCl_3$ (0·6 mol. per l.). With cotton-(I) and its rayon and other derivatives and linen-(I), t (corr. for the induction period of 0·4 hr.) $\propto C$, but with wood-(I) and its rayons the curves consist of two linear portions of different slopes. They indicate that on hydrolysis the formation of hydrocellulose results in a loss of available glucose; that mercerisation of cotton or dispersion of it in $Cu(NH_3)_4^{\cdot\cdot}$ increases the availability of glucose by increasing the amount of non-resistant (I) above the normal ~10%; and that the proportion of easily hydrolysed material in wood-(I) is > in cotton-(I). The theory that (I) consists entirely of chains of anhydroglucose units in various degrees of association, from a dense cryst. to an amorphous easily hydrolysed fraction, is confirmed. J. G.

Depolymerised cellulose and its hydrolysis. A. Buevskoi (*J. Appl. Chem. Russ.*, 1940, **13**, 1649—1659).—Depolymerisation is effected by treatment with 65—80% H_2SO_4 at −13° and 20°. The mol. wt. of the products falls with increasing [H_2SO_4], temp., and duration of contact. Products of the mol. wt. 83,400 to 505 were isolated by fractional pptn. methods. The velocity of hydrolysis of the depolymerisation products is independent of their mol. wt.; it is, however, $\propto$ their solubility, rising abruptly with transition to homogeneous systems. R. T.

Manufacture of primary amines.—See B., 1941, II, 294.

Configurational relationships of aliphatic amines. P. A. Levene and M. Kuna (*J. Biol. Chem.*, 1941, **140**, 259—265).—α-Methylheptoic acid, $[\alpha]_D^{25}$ −7·8°, yields successively the chloride, b.p. 67—70°/12 mm., $[\alpha]_D^{25}$ −5·1°, and nitrile, b.p. 71—73°/14 mm., $[\alpha]_D^{25}$ −14·9°, and α-amino-β-methylheptane, b.p. 105—106°/113 mm., $[\alpha]_D^{25}$ +3·04° (hydrochloride, $[\alpha]_D^{25}$ +2·0° in H_2O) (with the *sec.* amine, b.p. 90—100°/1 mm., $[\alpha]_D^{25}$ +0·56°). n-C_5H_{11}·CHMe·$[CH_2]_3$·Br, $[\alpha]_D^{27\cdot5}$ +2·5°, with KCN yields δ-methyldeconitrile, b.p. 106—110°/11 mm., $[\alpha]_D^{25}$ +1·46°, reduced (Raney Ni) to inactive α-amino-ε-methyldecane (inactive hydrochloride). α-Ethylhexoic acid, $[\alpha]_D^{25}$ −3·54°, yields successively the chloride, b.p. 62—64°/10 mm., $[\alpha]_D^{25}$ −1·63°, and nitrile, b.p. 98—100°, $[\alpha]_D^{26}$ −4·80°, and α-amino-β-ethylhexane, b.p. 98—99°/90 mm., $[\alpha]_{5875\cdot6}^{25}$ −0·52° (hydrochloride, $[\alpha]_{5875\cdot6}^{25}$ −1·07° in H_2O). *d*-Nonan-δ-ol, b.p. 94—95°, $[\alpha]_D^{25}$ +0·57°, yields successively 1-δ-*iodo-*, b.p. 98—99°/12 mm., $[\alpha]_D^{25}$ −1·72°, *-azido-*, b.p. 100°/23 mm., $[\alpha]_D^{25}$ −0·1°, and *-amino-nonane*, b.p. 113—114°, $[\alpha]_{5461}^{25}$ +0·52° (A., 1937, II, 447) (hydrochloride, $[\alpha]_{5461}^{25}$ −0·94° in H_2O). Rotations of some configurationally related amines are tabulated. [α] are homogeneous except where otherwise stated. A. Li.

Manufacture of quaternary ammonium compounds.—See B., 1941, II, 250.

Preparation of β-ethylaminoethanols.—See B., 1941, II, 295.

Manufacture of monosodium glutamate from gluten.—See B., 1941, II, 296.

Chondrosin. P. A. Levene (*J. Biol. Chem.*, 1941, **140**, 267—277).—*Chondrosin Me ester hydrochloride* (I), m.p. 165—170°, $[\alpha]_D^{30}$ +39·2° in MeOH, is reduced (Raney Ni under pressure) to Me *d*-chondrosaminido-*l*-gulonate; the N-*Ac* derivative of the *hepta-acetate* (Ac_2O in C_5H_5N), m.p. 122°, $[\alpha]_D^{25}$ −21·3° in EtOH, is methylated (Me_2SO_4, then CH_2N_2, then MeI–Ag_2O) to *Me* N-*acetyl*-d-*chondrosaminido*-l-*gulonate Me*$_7$ *ether*, m.p. 67°, $[\alpha]_D^{25}$ −4·8° in EtOH, reduced (Cu chromite at 175° under pressure) to N-*acetyltrimethylchondrosaminido-tetramethylsorbitol*, m.p. 55—57, $[\alpha]_D^{30}$ −44·2° in $CHCl_3$. The N-*acetylhexa-acetate* (Ac_2O + NaOAc), m.p. 99—100° (softening at 98°), $[\alpha]_D^{25}$ +12·2° in $CHCl_3$, of (I) is methylated (as above) to N-*acetylhexamethylchondrosin Me ester*, a syrup, $[\alpha]_D^{25}$ −5·2° in $CHCl_3$. A. Li.

Methionine and its derivatives. I. Detection. Y. Tsuchiya (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 465—475).—When MeSH is passed into a solution of 0·01—0·02 g. of isatin in 100 c.c. of conc. H_2SO_4 the yellow colour of the solution becomes grass-green. The reaction is inhibited by H_2S. 0·2 mg. of methionine (I) can be detected as follows by this reaction : 0·2—100 mg. of dried sample, mixed with 0·45—0·75 g. of NaOH and a little H_2O, is fused for 1—2 min. The melt is treated with dil. acid and the gases evolved are passed over $Pb(OAc)_2$ and then through the special reagent. Among the naturally occurring NH_2-acids only (I) gives the reaction, which is not given by mixtures of NH_2-acids and carbohydrates. A mixture of cystine and betaine gives the reaction and also compounds which contain the SMe group

such as SMe·$[CH_2]_2$·CH(OH)·CO_2H, SMe·$[CH_2]_3$·NH_2, and SMe·$[CH_2]_3$·OH; oxidised derivatives of (I) such as methionine sulphoxide, homocystine, and β-methylsulphonylpropionic acid yield only H_2S and do not give the reaction, which appears to be sp. for MeSH. J. N. A.

Synthesis of the aspartic acid analogue of glutathione (asparthione). G. M. Miller, O. K. Behrens, and V. Du Vigneaud (*J. Biol. Chem.*, 1941, **140**, 411—415).—*N*-Carbobenzyloxy-α-benzylaspartyl chloride and *S*-benzylcysteinylglycine Me ether in $CHCl_3$ at room temp. afford *N-carbobenzyloxy-α-benzyl-β-aspartyl*-S-*benzylcysteinylglycine Me ether*, m.p. 153°, hydrolysed (N-NaOH in dioxan) to the *acid*, m.p. 168—170°. This is converted by Na in liquid NH_3 into *β-aspartylcysteinylglycine* (*asparthione*), $[\alpha]_D^{25}$ −29·0° in H_2O. H. W.

Production of urea from ammonia and carbon dioxide containing inerts.—See B., 1941, II, 295.

Dimorphism of bromodiethylacetylcarbamide. A Watanabe (*J. Pharm. Soc. Japan*, 1940, **60**, 163—164).—Bromodiethylacetylcarbamide is obtained as a rhombic holohedral variety (*A*) by slow crystallisation of technical adalin (I) from MeOH or $COMe_2$ and as a monoclinic holohedral form (*B*), m.p. 118°, by rapidly cooling a somewhat more conc. solution of (I); crystallographic and optical data are recorded. *A* and *B* are stable at room temp. but at 70° *A* passes rapidly into *B* so that its true m.p. cannot be determined. *A* and *B* have the composition, $C_7H_{13}O_2N_2Br$. H. W.

Oxidising action of selenious acid. I. Organic sulphur compounds. A. E. A. Werner (*Sci. Proc. Roy. Dublin Soc.*, 1941, **22**, 387—392).—Mono-, di-, and tri-alkyl- and monoacylthiocarbamides, and thioamides with H_2SeO_3 give Se or Se + S. Strong acid suppresses the formation {by decomp. of [NRR′·C(NR″)·S]$_2$} of S, and in very strongly acid solutions no reduction occurs. Diacetylthiocarbamides react only in strongly acid solution. In EtOH or weak acid, thioalcohols give no ppt., thioacids a complex of H_2SeO_3 with the thioacid, but in very strongly acid solutions both give Se. Compounds containing S but not SH do not reduce H_2SeO_3. The significance of these results is discussed. A. Li.

Synthesis of methylenediureide and its polymeride-homologues. A. A. Vanscheidt, Z. K. Naumova, and E. P. Melnikova (*J. Gen. Chem. Russ.*, 1940, **10**, 1968—1972).—$CH_2(NH·CO·NH_2)_2$ condenses with CH_2O in aq. Ba(OH)$_2$ to the *compound*, $CH_2(NH·CO·NH·CH_2·OH)_2$, which with $CO(NH_2)_2$ in dil. HCl at room temp. yields the *compound*, $CO(NH·CH_2·NH·CO·NH_2)_2$, m.p. 227°, with $CH_2(NH·CO·NH·CH_2·NH·CO·NH_2)_2$. R. T.

Preparation of aceto- and benzo-nitriles. Y. S. Gwan (*J. Indian Chem. Soc.*, 1941, 18, 164).—NH_2Ac and NH_2Bz with *p*-$C_6H_4Me·SO_2Cl$ at 130—135° give good yields of the nitriles. A. Li.

Synthesis of succinonitrile.—See B., 1941, II, 251.

Action of olefine oxides on halides of arsine. II. M. S. Malinovski (*J. Gen. Chem. Russ.*, 1940, **10**, 1918—1922).—$AsCl_3$ saturated at room temp. with $(CH_2)_2O$ yields *tri-(β-chloroethyl) arsenite*, b.p. 190—195°/8 mm., with *di-(β-chloroethoxy)arsine chloride*, b.p. 168—175°/10 mm., and *β-chloroethoxyarsine dichloride*, b.p. 125—135°/10 mm. Epichlorohydrin (I) and $AsCl_3$ (10 days at room temp.) afford *tri-(β-chloro-α-chloromethylethyl) arsenite*, b.p. 188—193°/10 mm., and *β-chloro-α-chloromethylethoxyarsine dichloride*, b.p. 105—120°/10 mm. Propylene oxide (II) and $AsCl_3$ (10 days at room temp.) yield *di-(β-chloropropoxy)arsine chloride*, b.p. 185—190°/5 mm. $AsPhCl_2$ and $(CH_2)_2O$ (10 days at room temp.) afford *phenyldi-(β-chloroethoxy)arsine*, b.p. 190—193°/5 mm. $AsPhCl_2$ and (I) or (II) (10 days at room temp.) yield *phenyl-β-chloro-α-chloromethylethoxyarsine chloride*, b.p. 218—222°/5 mm., or *phenyl-β-chloropropoxyarsine chloride*, b.p. 190—195°/10 mm. R. T.

Co-ordinated mercury compounds with ethylene- and propylene-diamines. P. Neogi and K. L. Mondal (*J. Indian Chem. Soc.*, 1941, **18**, 146—148).—Equimol. amounts of $NH_2·[CH_2]_2·NH_2$ (pn) and Hg salts in EtOH yield H_2O-insol. *propylenediaminemercuric chloride*, m.p. >250° (decomp.), *bromide*, and *nitrate*. $NH_2·[CH_2]_2·NH_2$ salts with Hg salts in H_2O or EtOH yield H_2O-sol. *compounds*, [Hg(pn),2HCl]Cl_2, [Hg(pn),2HBr]Br_2, [Hg(pn),2HI]I_2, and [Hg(pn),2HNO$_3$](NO$_3$)$_2$. $NH_2·[CH_2]_2·NH_2$,2HNO$_3$ similarly yields compounds [Hg(en)](NO$_3$)$_2$ and [Hg(en),2HNO$_3$](NO$_3$)$_2$. A. Li.

II.—HOMOCYCLIC.

***cyclo*Hexene derivatives.**—See B., 1941, II, 251.

Distribution of multiple linkings in ring systems. IV. Six-membered rings with the allene system of linkings. N. A. Domnin (*J. Gen. Chem. Russ.*, 1940, **10**, 1939—1949).—2′-Methyl*cyclo*hexanone in light petroleum and PCl_5 yield 2 : 2-*dichloro*-1-*methyl*cyclo*hexanone*, b.p. 62—64°/8 mm., which with 20% KOH in EtOH (5 hr. at the b.p.) affords 2-*chloro*-1-*methyl*-Δ^1-cyclo*hexene*, b.p. 44°/9 mm. This is chlorinated in $CHCl_3$ in presence of $NaHCO_3$ to 1 : 2-*dichloro*-1-*methyl*-Δ^2-cyclo*hexene*, b.p. 80—82°/8 mm., and 1 : 2 : 2-*trichloro*-1-*methyl*cyclo*hexane*, b.p. 100—102°/8·5 mm. R. T.

Benz*cyclo*octatetraenes. I. W. S. Rapson and R. G. Shuttleworth (*J.C.S.*, 1941, 487—490).—*o-Iodobenzanilide*, m.p. 142·5°, and PCl_5–PhMe, followed by $SnCl_2$–HCl–Et_2O (ice-cooling), afford *o*-$C_6H_4I·CHO$ (I), converted by $CH(OEt)_3$–EtOH–NH_4Cl into its Et_2 acetal, b.p. 159°/23 mm. (I) and Cu-bronze in an inert atm. at 200—220° give diphenyl-2 : 2′-dialdehyde, m.p. 63°, but attempts to prepare 1 : 2 : 3 : 4-dibenz-Δ$^{1:3:5:7}$-*cyclo*octatetraene (II) from it by reaction with succinic acid or Et_2 succinate failed. *o*-Iodocinnamaldehyde [from (I) and MeCHO in EtOH–$NHEt_2$] and *o*-$C_6H_4I·CH_2·CO_2H$ (improved prep.) (*Et* ester, m.p. 42—43°) with PbO–Ac_2O at 150—160° give *αδ-bis-o-iodophenyl-Δ$^{\alpha\gamma}$-butadiene* (III), isomerides, m.p. 249—250° (III) and 180—181° (IV), not converted into (II). (III) and Cu-bronze alone at 280° or in a little boiling quinoline yield intermol. condensation products (a *substance*, $C_{32}H_{24}I_2$, m.p. 200—202°, is isolable); in more dil. solution *trans-αδ*-diphenyl-Δ$^{\alpha\gamma}$-butadiene is formed. Cu-bronze and (IV) at 300° in an inert atm. (no reaction in quinoline) afford a *product*, ? $C_{48}H_{36}I_2$, m.p. ~200°. 2 : 2′-Dibromodiphenyl and Na give Ph_2 (cf. Mascarelli *et al.*, A., 1934, 62). CHNaAc·CO_2Et and *o*-$C_6H_4I·COCl$ in Et_2O yield a product, hydrolysed by dil. H_2SO_4 to *o*-$C_6H_4I·COMe$, b.p. 112°/4 mm. (*semicarbazone*, m.p. 178·5—179·5°), and *o*-$C_6H_4I·CO_2Et$, b.p. 122°/4 mm., in approx. equimol. proportions. A. T. P.

Condensation of alcohols with aromatic hydrocarbons in presence of aluminium chloride. Condensation of *cyclo*heptanol with benzene and toluene. N. G. Sidorova and I. P. Tzukervanik (*J. Gen. Chem. Russ.*, 1940, **10**, 2073—2076).—Suberol and C_6H_6 condensed in presence of $AlCl_3$ yield cyclo*heptylbenzene*, b.p. 132—135°/28 mm., nitrated to p-*nitro*cyclo*heptylbenzene*, b.p. 203—210°/38 mm., from which p-cyclo*heptylaniline*, an oil (*Bz*, m.p. 173°, and *Ac* derivative, m.p. 136—137°), is prepared. With PhMe suberol yields a mixture of m- and p-cyclo*heptyltoluene*. R. T.

Polymerisation of styrene in heavy alcohol. (Mechanism of chain polymerisation of styrene in solution.) T. Yosida and T. Titani (*Bull. Chem. Soc. Japan*, 1941, **16**, 125—136).—Exchange of H of CHPh:CH_2 (I) or polystyrene is not observed when freshly prepared (I) (2 c.c.) is heated in a sealed tube for 22 hr. at 130° with 3·6% or 10·4% EtOD or with 9·8% or 11·5% $C_2H_4D·OH$. The mechanism of polymerisation is discussed. J. L. D.

Free aryl radicals in the Fittig and Ullmann reactions. W. S. Rapson and R. G. Shuttleworth (*Nature*, 1941, **147**, 675).—A series of Ullmann, Fittig, and related reactions showed that one of the products formed on treating ArX (X = Cl, Br, or I) with Na or Cu is the compound, ArH. This is attributed to the formation of free aryl radicals in the reaction, from which ArH is formed either by reaction with the diluent when present, or by dismutation when the diluent is absent. The isolation of diphenyl-2- and -4-carboxylic acids from the reaction between PhI and EtOBz in presence of Cu-bronze supports this view. L. S. T.

Electrolysis of iodonium compounds. Attempt to prepare iodonium amalgam. E. V. Zappi and R. Mastropaolo F. (*Anal. Asoc. Quím. Argentina*, 1941, **29**, 88—94).—No amalgam is obtained by electrolysis, at 4·5 v. and 0° with an agitated Hg cathode, of diphenyl-, *o*- and *p*-dianisyl-iodonium hydrates. The products isolated consist of the corresponding aryl iodide and diaryl. F. R. G.

Velocity of decomposition of naphthalene, tetra- and deca-hydronaphthalene, and dodecane during destructive hydrogenation.—See A., 1941, I, 421.

Preparation of α-chloro-αββ-triphenylethylene. W. Tadros (*Nature*, 1941, **148**, 53).—SO_2Cl_2 (35 g.), CPh_2:CHPh (prep. described) (50 g.) in CCl_4 (25 c.c.), and Bz_2O_2 (0·2 g.) are refluxed on a water-bath for 45 min. Excess of SO_2Cl_2 is removed by distillation under reduced pressure, and the oily residue recryst. twice from EtOH. The mother-liquors are conc., and the oil that separates is recryst. from EtOH. The yield of CPh_2:CClPh, m.p. 117°, is 45 g. L. S. T.

Certain peculiarities of reactions involving formation of conjugated double linkings. Preparation of δε-diphenyl-Δ$^{\alpha\gamma\epsilon\eta}$-octatetraene from γ-benzoylpropyl bromide. S. N. Chitrik (*J. Gen. Chem. Russ.*, 1940, **10**, 2095—2097).—Bz·$[CH_2]_3$·Br and Na–Al in moist Et_2O yield *αθ-dibromo-δε-diphenyloctane-δε-diol*, m.p. 160—161°, converted by fusion in presence of sulphanilic acid into *δε-diphenyl-Δ$^{\alpha\gamma\epsilon\eta}$-octatetraene*, m.p. 84—85°. R. T.

Preparation of methyl halide [halogenomethyl] derivatives of aromatic hydrocarbons.—See B., 1941, II, 297.

Nitrous acid as a nitrating and oxidising agent. IV. *N*-Dialkylanilines. H. H. Hodgson and D. E. Nicholson (*J.C.S.*, 1941, 470—475; cf. A., 1936, 1501).—The behaviour of *N*-dialkylanilines towards excess of HNO_2 (2 or 5 times that required for nitrosation) in 5% or 15—16% HCl at 0° is studied. $NPhMe_2$ thus gives a 3 : 1 mixture of solid *p*-NO·C_6H_4·NMe_2,HCl (**I**) and *p*-NO_2·C_6H_4·NMe_2; the filtrate, when kept, affords *p*-NO_2·C_6H_4·NMe·NO (**II**), a little 2 : 5 : 1-$(NO_2)_2C_6H_3$·NHMe (indicates some *m*-nitration), and still less (?) $(NO_2)_3C_6H_2$·NMe_2. *p*-Nitrosation and *p*-nitration are considered to be simultaneous initial reactions. $NPhEt_2$ readily affords *p*-NO_2·C_6H_4·NEt·NO (**III**), whilst NHPhMe(Et) afford the respective *N*-NO-derivative, and thence (**II**) [or (**III**)]. NPhMeEt affords p-*nitrosomethylethylaniline*, m.p. 69°, converted on long keeping (with HNO_2) into (**II**) + (**III**) (~83 : 17). CH_2Ph·NPhMe (in aq. HCl–AcOH–$NaNO_2$) gives a mixture of 4-nitro- (**IV**) and some 2 : 4-dinitro-benzylmethylaniline (**V**), the former being converted by HNO_2 into (mainly) (**V**) and a little *p*-NO_2·C_6H_4·N(NO)·CH_2Ph (**VI**). (**V**) and boiling conc. HCl yield 2 : 4 : 1-$(NO_2)_2C_6H_3$·NHMe, whereas (**IV**) is similarly unchanged. CH_2Ph·NPhEt readily reacts to give (**VI**). In no case is the CH_2Ph group expelled by HNO_2 and Et is more readily removed than is Me. An improved prep. of (**I**) is described. A. T. P.

Production of diarylamines.—See B., 1941, II, 332.

Cu and Co^{III} 1-nitroso-β- and 2-nitroso-α-naphthylamine.—See A., 1941, I, 429, 430.

N^1-β-Aminoethyl- and N^1-β-diethylaminoethyl-sulphanilamide. L. H. Amundsen and L. A. Malentacchi (*Science*, 1941, **93**, 286).—*p*-NHAc·C_6H_4·SO_2Cl with NHAc·CH_2·CH_2·NH_2 and NEt_2·CH_2·CH_2·NH_2 in $CHCl_3$ + aq. $NaHCO_3$ followed by hydrolysis (6N-HCl) gives N^1-*β-aminoethyl-* and N^1-*β-diethylaminoethyl-sulphanilamide dihydrochloride*, m.p. 217—220° (decomp.) and 190—195° (decomp.), respectively. L. S. T.

Sulphanilylguanidine. T. Dewing and S. Smith (*Nature*, 1941, **148**, 24).—Fusion of sulphanilamide with dicyanodiamide gives sulphanilylguanidine and not phenylguanidine-4-sulphonamide (cf. A., 1938, III, 937; Marshall *et al.*, A., 1941, III, 786). L. S. T.

Theory of aromatic substituents and rearrangement with special reference to the benzidine change. E. D. Hughes and C. K. Ingold (*J.C.S.*, 1941, 608—613; cf. A., 1926, 833).—Views expressed previously are modified. With the recognition of the quantal theory of mesomerism, theories involving "chronology" of electron displacements (those which specify a succession of electron displacements in an identical nuclear framework) are superseded. The mechanism of the benzidine rearrangement is discussed (cf. A., 1933, 1044; Robinson, *J.C.S.*, 1941, 220). An argument against homolysis of the N–N bond is that the benzidine change does not occur under conditions in which this form of dissociation is known to be considerable; heterolysis is assumed. Homolysis and heterolysis refer to bond fission according to schemes X·|·Y and X|··Y, respectively (dots denote shared electrons), independently of states of electrification of X and Y and any concomitant covalency changes. The transition state, although largely ionic, is partly covalent; the electronic system of the transition state is examined in detail. Stereochemical aspects of the benzidine change are discussed, and also the nature of the semidine rearrangement. A. T. P.

Comparison of hydrogenation of aliphatic and alicyclic azines. I. Azines of hexahydrobenzaldehyde and heptaldehyde. II. Azines of *cyclo*hexanone and ethyl propyl ketone. P. G. Ugriumov (*J. Gen. Chem. Russ.*, 1940, **10**, 1985—1994, 1995—1998).—I. Hexahydrobenzaldehyde and N_2H_4 yield the *azine* (**I**), b.p. 140—141°/3 mm., 166—167°/11 mm. The velocity of hydrogenation (Pt-black in EtOH) of (**I**) is considerably < of diheptylideneazine (**II**); the chief product formed is NN′-*dihexahydrobenzylhydrazine*, b.p. 140—142°/3 mm. [*hydrochloride*, m.p. 193—194°; *dihydrochloride*, m.p. 205—206° (decomp.); NN′-*Bz*$_2$ derivative, m.p. 146—146·5°], oxidised by PbO in Et_2O to *ω-azohexahydrotoluene*, $(:N·CH_2·C_6H_{11})_2$, b.p. 116—117°/3 mm., 164—166°/18 mm. (**II**) similarly yields NN′-*di*-n-*heptylhydrazine*, b.p. 118—119°/3 mm. (*dihydrochloride*, m.p. 160—170°; NN′-*Bz*$_2$ derivative, m.p. 48—49°), oxidised to *α-azoheptane*, $(:N·C_7H_{15})_2$, b.p. 110—111°/2·5 mm., 144—145°/17 mm.

II. The velocity of hydrogenation of *cyclo*hexanoneazine is slightly > of $(CEtPr:N)_2$, which yields NN′-*diethyl*-NN′-*di*-n-*propylhydrazine*, b.p. 99·5—100°/10 mm. R. T.

Diazo-compounds. IV. Effect of polyhydric alcohols and of certain carbohydrates on tetrazotisation of *m*-phenylenediamine. V. V. Kozlov and B. I. Stepanov (*J. Gen. Chem. Russ.*, 1940, **10**, 1510—1523).—The yield of tetrazonium derivative obtained from *m*-$C_6H_4(NH_2)_2$ in presence of polyhydric alcohols (*A*) rises with increase in the no. of OH in the mol. of, and with increasing concn. of, (*A*). At the same mol. concn. the effect of various (*A*) increases in the order glycol < glycerol < glucose < mannitol < maltose < sucrose < raffinose. R. T.

Structure and properties of the so-called *p*-diazoimines. A. M. Simonov (*J. Gen. Chem. Russ.*, 1940, **10**, 1220—1229).—The following mesomerism of diazoimines is suggested: $NR·C_6H_4·N:N \rightleftharpoons NR:C<^{CH:CH}_{CH:CH}>C<^{N}_{N}$, in which the second mesomeride is bipolar. Coupling with OH-compounds takes place in the same way as with ordinary diazo-compounds. The following are described: *compounds* of 2′ : 4′-dinitro-4-diazodiphenylamine (**I**) with *α*-$C_{10}H_7$·NH_2, m.p. 257—258°, with $CH_2Ac·CO_2Et$, m.p. 203·5—204°, with $CH_2Ac·CO·CO_2Et$, m.p. 180·5—182·5° (decomp.), and with 1-phenyl-3-methyl-5-pyrazolone, m.p. 283°. (**I**) and *p*-O:C_6H_4:O in aq. NaOAc at 30° yield 2-(p-2′ : 4′-*dinitroanilinophenyl*)-p-*benzoquinone*, m.p. 241·5—242·5°. 2′ : 4′-*Dinitro-4-dimethylaminodiphenylamine methiodide*, m.p. 182° (decomp.), is readily converted by KOH in MeOH into the *compound*, 2 : 4 : 1-$(NO_2)_2C_6H_3·\bar{N}·C_6H_4·\overset{+}{N}Me_3$, m.p. 218·5—220° (decomp.). R. T.

Alkylpyrocatechols.—See B., 1941, II, 333.

Co^{II} dinitroso-resorcinol and -orcinol and Co^{III} oximinodimedone.—See A., 1941, I, 430.

Syntheses of stilbene derivatives. II. Synthesis of *trans*-4 : 4′-dihydroxy-αβ-diethylstilbene. S. Kuwada, Y. Sasagawa, and M. Nisikawa (*J. Pharm. Soc. Japan*, 1940, **60**, 224—226; cf. A., 1940, II, 215).—OH·CHEt·COEt and *p*-OMe·C_6H_4·MgBr (**I**) give *γδ-dihydroxy-γ-p-anisylhexane*, b.p. 143—144°/0·5 mm., m.p. 83—84° (*monoacetate*, m.p. 101—102°), isomerised by hot 30% H_2SO_4 to *γ-p-anisylhexan-δ-one*, b.p. 140—155°/14 mm. (*oxime*, m.p. 133·3°). This and (**I**) afford γδ-di-*p*-anisylhexan-γ-ol, m.p. 115—117°, which is dehydrated to γδ-di-*p*-anisyl-Δ$^{\gamma}$-hexene, demethylated (Späth) to γδ-di-*p*-hydroxyphenyl-Δ$^{\gamma}$-hexene (*trans*-4 : 4′-dihydroxy-αβ-diethylstilbene). H. W.

4 : 5-Methylenedioxychrysene. L. H. Briggs and (Miss) J. M. Wilson (*J.C.S.*, 1941, 500—501).—α-$C_{10}H_7$·CH_2·CO_2K and 6-nitropiperonal in Ac_2O at 100° give *2-nitro-*, m.p. 203·5—206·5°, and thence [Fe(OH)$_2$–aq. NH_3] *2-amino-4 : 5-methylenedioxy-α-1′-naphthylcinnamic acid*, m.p. 161·5—163·5° (decomp.), which when diazotised (H_2SO_4–C_5H_{11}·O·NO at 25—30°) and treated with Cu powder + Cu-bronze in aq. NaH_2PO_2 at 45° to b.p. gives a crude acid, decarboxylated (Cu-bronze at 200—240°/0·04 mm.) to 4 : 5-*methylenedioxychrysene*, m.p. 222—223° (picrate, m.p. 202—202·5°). A. T. P.

Sinomenine. XLVIII. Degradation of sinomenolquinone dibenzoate to 2 : 3 : 3′ : 4′-tetramethoxydiphenyl. K. Goto and H. Shishido (*Bull. Chem. Soc. Japan*, 1941, **16**, 170—172).—Sinomenolquinone dibenzoate (cf. A., 1929, 1187) and H_2O_2 in warm AcOH give 5 : 6′-*dibenzoyloxy*-4 : 5′-*dimethoxydiphenic acid*, m.p. 233—235° (decomp.) (*Me*$_2$ ester, m.p. 170—173°), converted by hot KOH–MeOH–H_2O in H_2 and then Me_2SO_4–KOH into 4 : 5 : 5′ : 6′-*tetramethoxydiphenic acid*, m.p. 206—208° (could not be resolved; *Me*$_2$ ester, sinters at 124°, m.p. 132°), which with Cu powder in quinoline at 240—250° gives 2 : 3 : 3′ : 4′-*tetramethoxydiphenyl*, m.p. 96—100°. R. S. C.

2 : 4-Dinitro-5-naphthylaminophenols.—See B., 1941, II, 332.

4 : 6-Diamino-3-methoxytoluene. K. I. Bogatscheva (*J. Appl. Chem. Russ.*, 1940, **13**, 1606—1607).—4 : 6 : 1 : 3-$(NO_2)_2C_6H_2Me$·OMe is reduced by Fe in aq. EtOH–HCl (1 hr. at the b.p.) to 4 : 6-*diamino*-3-*methoxytoluene*, m.p. 101°; with H_2SO_4–HNO_3 at 120° it yields 2 : 4 : 6-*trinitro*-3-*methoxytoluene*, m.p. 92°. R. T.

Ephedrine alkanesulphonates.—See B., 1941, III, 269.

Action of alkali on chemical and physiological properties of adrenaline. F. H. Shaw (*Austral. J. Exp. Biol.*, 1941, **19**, 151—155).—During the action of alkali on adrenaline (I) an intermediate is rapidly formed which is probably the corresponding *o*-quinone; it retains the physiological activity of (I). After 2—5 min. action, the physiological activity has disappeared; the final product is not adrenochrome and its exact nature is unknown. D. M. N.

Physico-chemical study of products of oxidation of adrenaline. I. Isolation of adrenochrome. J. S. Rozum and S. S. Urazovski (*J. Gen. Chem. Russ.*, 1940, **10**, 1573—1579).—Adrenochrome is shown by chromatographic analysis to be a mixture of $\not<$ 7 substances. Of these, a brown substance predominates. At any given p_H a state of dynamic equilibrium exists between all these substances. R. T.

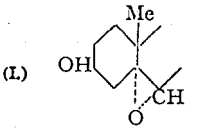
Sterols. XXII. Identity of bessisterol and spinasterol. S. Kuwada and S. Yosiki (*J. Pharm. Soc. Japan*, 1940, **60**, 161—162; cf. A., 1940, II, 218).—Comparison of α-spinastenol, spinastanol, and spinastanone and their derivatives with the corresponding compounds from α-bessistaenol establishes the identity of bessisterol with spinasterol. H. W.

Sterols. XXIII. Sterol from the seeds of *Momordica Cochinchinensis*, Spreng. S. Kuwada and S. Yosiki (*J. Pharm. Soc. Japan*, 1940, **60**, 232—233).—Extraction of the seeds with Et_2O followed by hydrolysis of the extract and purification of the unsaponifiable matter (*A*) through the 3 : 5-dinitrobenzoate and then chromatographically (Al_2O_3) leads to the isolation of a sterol, $C_{28}H_{48}O$, m.p. 156·5—163·5°, $[\alpha]_D^{22}$ +5·81°. Chromatography with the crude cryst. material from (*A*) gives a sterol, $C_{28}H_{48}O$·0·5H_2O, m.p. 163·5—167·5°, $[\alpha]_D^{22}$ +4·04° (acetate, m.p. 174·5—176·5°; benzoate, m.p. 196—198°), probably identical with cucurbitasterol (Lendle, A., 1938, III, 358). M.p. are corr. H. W.

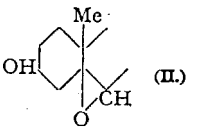
Pentacyclic steroids. O. Rosenheim (*Nature*, 1941, **147**, 776—777).—Transannular tautomeric changes explain some of the reactions of *cis*-Δ^5-cholestene-3 : 4-diol, the formation of *i*-cholesterol from cholesterol, and the migration of Bz in 6-chloro-3-benzoyloxy-Δ^4-cholestene. L. S. T.

α-Œstradiol dimethyl and 17-methyl ether and related compounds. Y. Urushibara and T. Nitta (*Bull. Chem. Soc. Japan*, 1941, **16**, 179—182).—Figures given in parentheses below are min. œstrogenic doses (rats; μg. in oil). The Na derivative of α-œstradiol 3-Me ether (I) (4—5), m.p. 95—97°, and Me_2SO_4 in boiling Et_2O and later C_6H_6 give the *Me*$_2$ *ether* (<10, >5), m.p. 161—162°, also obtained from œstrone Me ether (15), Na, and Me_2SO_4 in C_6H_6 and converted by HI–AcOH into α-œstradiol 17-Me ether (<2·5), m.p. 213·5—214·5° (3-benzoate, m.p. 165·5—166·5°; 3-*p*-toluenesulphonate, m.p. 124·5—125·5°). (I) gives the 17-acetate, m.p. 103·5—104·5°, 17-benzoate, m.p. 131—132°, and 17-*p*-toluenesulphonate, m.p. 160—161°. α-Œstradiol 17-*p*-toluenesulphonate (~100), m.p. 171—172°, di-*p*-toluenesulphonate, m.p. 172—173°, and 3-benzoate 17-*p*-toluenesulphonate, m.p. 184·5—185·5°, are prepared. Min. effective doses are œstrone 2 and diethylstilbœstrol 0·5 (Me$_2$ ether 5) μg. Duration of œstrus is recorded for numerous compounds. M.p. are corr. R. S. C.

Configurations of cholesterol oxides, Δ^4-cholestene- and cholestane-3 : 6-diols. Y. Urushibara (*Bull. Chem. Soc. Japan*, 1941, **16**, 182—185).—Known reactions establish configurations as follows. Cholesterol α- (I), m.p. 140—141°, and β-oxide (II), m.p. 136°; 5(β)-chloro-6(β)-hydroxycoprostan-3(β)-ol = "5-chloro-6-hydroxycholestanol"; Δ^4-cholestene-3(β) : 6(β)-, m.p. 257—258°, and -3(β) : 6(α)-diol, m.p. 178—179°; cholestane-3(β) : 6(β)-, m.p. 194—195°, and -3(β) : 6(α)-diol (III), m.p. 216°. This is confirmed by reduction of (I) to (III) by Na–C_5H_{11}·OH. R. S. C.



(I.)



(II.)

7-Hydroxy- and 7-keto-cholesterol.—See B., 1941, III, 269.

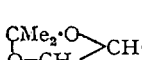
Recovery of pregnanediol.—See B., 1941, III, 269.

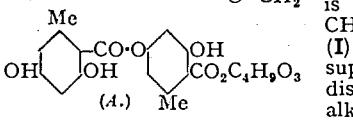
Zinc dust distillation of benzenoid compounds. Z. Nikuni, H. Hayashi, and S. Tsuji (*J. Agric. Chem. Soc. Japan*, 1941, **17**, 414—418).—Distillation of guaiac resinic acid [α-3-hydroxy-4-methoxyphenyl-δ-4-hydroxy-3-methoxyphenyl-βγ-dimethyl-Δ$^\alpha$-butene] with Zn dust in H_2 yields 2 : 3-$C_{10}H_6Me_2$ and anthracene (I). CHPh:CH·CO_2H yields small amounts of stilbene, whilst $CH_2Ph·CH_2·CO_2H$ yields a trace of (I) and much $C_{10}H_8$. $CH_2Ph·CO_2H$ yields distilbene and a trace of (I). In every case an unidentified yellowish oil is also formed. J. N. A.

Reaction of acraldehyde with anthracene. A. G. Slobodski and V. I. Chmelevski (*J. Gen. Chem. Russ.*, 1940, **10**, 1199—1201).—Anthracene and CH_2:CH·CHO in presence of aq. SO_2 (3 hr. at 130°) yield an oily product, oxidised by Ag_2O to *αβ-endo*-9 : 10-dihydroanthracene-9 : 10-propionic acid. R. T.

Chloralamides. X. Reactivity of α-halogen in α-halogenochloral-nitro- and -bromo-methoxybenzamides. N. W. Hirwe, (Miss) K. D. Gavankar, and B. U. Patil (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 371—373).—The customary reactions lead to the following: *α-chloro-*, m.p. 149—150°, *α-methoxy-*, m.p. 144°, *α-ethoxy-*, m.p. 146—147°, *α-anilino-*, m.p. 168—169°, *α-o-toluidino-*, m.p. 151—152°, and *α-p-toluidino-*, m.p. 171—172°, *-chloral-5-nitro-2-methoxybenzamide*; *α-chloro-*, m.p. 150—151°, *α-bromo-*, m.p. 140°, *α-ethoxy-*, m.p. 147—149°, *α-anilino-*, m.p. 168—169°, *α-o-toluidino-*, m.p. 166—167°, *α-p-toluidino-*, m.p. 175—177°, and *α-phenoxy-*, m.p. 191—192°, *-chloral-5-bromo-2-methoxybenzamide*; *α-chloro-*, m.p. 109—110°, *α-anilino-*, m.p. 166—167°, *α-o-toluidino-*, m.p. 166—167°, and *α-p-toluidino-*, m.p. 173—174°, *-chloral*-3 : 5-*dibromo*-2-*methoxybenzamide*; *α-methoxychloral*-3-*nitro*-2-*methoxybenzamide*, m.p. 104—105°. Chloral-3 : 5-dinitro-2-methoxybenzamide and PCl_5 appear to afford 3 : 5-*dinitro*-2-*methoxybenz-αβββ-tetrachloroethyl imidochloride*, m.p. 19°. H. W.

Constitution of erythrin. Y. Sakurai (*J. Pharm. Soc. Japan*, 1941, **61**, 45—46).—Erythrin (I), $C_{20}H_{22}O_{10}$ (also +1H_2O), m.p. 148°, from *Roccella montagnei* from Java or *R. sp.* from Zanzibar, is converted by NaOAc and boiling Ac_2O into a *hexa-acetate*, m.p. 85°, and by CH_2N_2 into a *Me*$_3$ *ether* (II), m.p. 111° (*triacetate*, m.p. 110°). (II), anhyd. $COMe_2$, and $CuSO_4$ slowly give iso*propylidene-erythrin Me*$_3$ *ether* (III), m.p. 65°, whereas (I) yields iso*propylidene-erythrin*, m.p. 105°; both substances readily afford $COMe_2$ in presence of cold mineral acid. (I) is insol. in alkali carbonate but sol. in alkali hydroxide, by which it is transformed at 40° into Me orsellinate (IV) and *r*-erythritol (V), whereas in boiling MeOH it gives (IV) and picroerythrin, m.p. 136·5° (lit. 158°), further methanolised to (IV) and (V). (II) is hydrolysed by KOH–EtOH to orsellinic acid Me$_2$ ether, *iso*evernic acid, and (V), thus establishing the depside nature of both orsellinic acid components. Carbethoxy*iso*evernyl chloride is reduced (Rosenmund) to the aldehyde, which is decarboxylated and coupled with orsellinyl chloride Me$_2$ ether to *lecanorylaldehyde Me*$_3$ *ether*, m.p. 131°, unusually sensitive to light. This is oxidised to the *acid*, m.p. 179°, the chloride of which with *iso*propylidene-erythritol (VI) in C_5H_5N gives (III) and

thence (II). (VI) is  CH·CH(OH)·CH$_2$·OH since it is oxidised by Pb(OAc)$_4$ to CH$_2$O and glyceraldehyde. (I) is therefore (*A*). The supposed conversion of (I) by dissolution in AcOH or in alkali with subsequent acidification into the so-called " erythric acid " is erroneous since these operations lead to unchanged (I). H. W.


(*A.*)

Preparation of diarylmaleonitriles. A. H. Cook, J. Downer, and B. Hornung (*J.C.S.*, 1941, 502—506).—2 : 1-OH·C$_{10}$H$_6$·CHO and Al–Hg in moist Et$_2$O afford (2 : 1-OH·C$_{10}$H$_6$)$_2$CH$_2$, 2 : 1-OH·C$_{10}$H$_6$·CH$_2$·OH, and a small amount of 2 : 2′-*dihydroxy*-1 : 1′-*dinaphthylethylene*, m.p. 252° [*Me$_2$ ether* (I), m.p. 222°]. 2-C$_{10}$H$_7$·OMe, (CH$_2$O)$_3$, and HCl–AcOH at <15° yield 2-*methoxy*-1-*chloromethylnaphthalene* (II), decomp. 120° (loses HCl); polymeric material is obtained at high temp. or from (II) at 120°. HCl is removed from (II) in COMe$_2$ by AgNO$_3$–EtOH at 30° to give s-2 : 2′-*dimethoxy*-1 : 1′-*dinaphthylethylene*, β-form, m.p. 145°; this and (I) are probably *cis*- and *trans*-isomerides. (II) and warm aq. COMe$_2$–NaHCO$_3$ afford 2 : 1-OMe·C$_{10}$H$_6$·CH$_2$·OH, whilst (II) and dil. KOH–EtOH at 40° yield 2-*methoxy*-1-*naphthylcarbinyl Et ether*, b.p. 173—175°/12 mm. (II) is converted by KCN–aq. COMe$_2$ at 30—35° into 2-*methoxy*-1-*naphthylacetonitrile* (III), m.p. 111° (*Br*-derivative, m.p. 145—146°, prep. by Br–CHCl$_3$), which does not give the corresponding diarylmaleonitrile with Br or I and bases. 2 : 1-OMe·C$_{10}$H$_6$·CH(OH)·CN and SOCl$_2$–C$_6$H$_6$ at room temp. yield *di*-2-*methoxy*-1-*naphthylcyanomethyl ether* (IV), m.p. 121°, whereas at higher temp. with excess of SOCl$_2$, or from (IV), 2-*methoxy*-1-*naphthylchloroacetonitrile*, m.p. 130°, is formed. The latter and warm C$_5$H$_5$N yield 2-*methoxy*-1-*naphthylcyanomethylpyridinium chloride*, m.p. 165° (slight decomp.), converted by aq. Na$_2$CO$_3$ into the orange 2-*methoxy*-1-*naphthylcyanomethylpyridinium enimine-betaine*, m.p. 150° (decomp.), which at 200°/0·001 mm. gives (III) and 2 : 2′-*dimethoxy*-1 : 1′-*dinaphthylmaleonitrile*, two stereoisomerides, α-, m.p. 255°, and β-, m.p. 290° (5% yield of each) (heating with Cu or Cu salts gives octanaphthylporphyrazines; FeCl$_3$ at 300° affords Fe porphyrazine pigments). *Cyanomethylpyridinium chloride* (V), m.p. 178°, and aq. K$_2$CO$_3$ or KOH give the corresponding betaine, which does not decompose to a nitrile; (V) and Bz$_2$O in CHCl$_3$–aq. K$_2$CO$_3$ yield ω-cyanophenacylpyridinium benzoate (cf. Kröhnke, A., 1939, II, 124). Neither (V) nor *acetamidopyridinium chloride*, m.p. 202—203°, gives any dimeric product on heating. CHClMe·CN affords a pyridinium salt and an unstable betaine. CHClPh·CN and C$_5$H$_5$N (2 days) give α-*cyanobenzylpyridinium chloride*, m.p. 159°, and thence the enimine-betaine, which at 120°/vac. yields diphenylmaleonitrile (~50% yield) (cf. Kröhnke, *loc. cit.*). Thus dimerisation appears to proceed only with arylhalogenoacetonitriles. CH$_2$Ph·CH(OH)·CN and PCl$_5$–C$_6$H$_6$ give α-*chloro*-β-*phenylpropionitrile*, b.p. 128—130°/13 mm., and thence the betaine, converted into cinnamonitrile. CHPh:CH·CH(OH)·CN and SOCl$_2$ give α-chloro-γ-phenyl-Δ$^{\beta}$-butenonitrile (no characteristic pyridinium salt or betaine is obtained), which when kept affords (probably) 2 : 5-*diphenyldihydroterephthalonitrile*, m.p. 114°. *p*-OMe·C$_6$H$_4$·CH(OH)·CN and SOCl$_2$ yield α-*chloro*-α-p-*anisylacetonitrile*, b.p. 153—155°/13 mm.; the pyridinium salt decomposes to *di*-p-*anisylmaleonitrile*, m.p. 186—187°, which gives a porphyrazine with Fe at 280—300°. 2 : 1-C$_{10}$H$_6$Me·CH$_2$Cl and KCN–85% EtOH give 2-*methyl*-1-*naphthylacetonitrile*, m.p. 78°; in presence of much H$_2$O, 2-*methyl*-1-*naphthylcarbinol*, m.p. 137—138°, is formed. A. T. P.

Phthalic anhydride.—See B., 1941, II, 334.

Preparation of substituted phthalic anhydrides.—See B., 1941, II, 334.

Preparation of phenylacetaldehyde. A. K. Schumeiko (*J. Appl. Chem. Russ.*, 1941, **14**, 93—95).—Ph·[CH$_2$]$_2$·OH in C$_6$H$_6$ or PhMe is oxidised by K$_2$Cr$_2$O$_7$–H$_2$SO$_4$ (30 min. at room temp.) to CH$_2$Ph·CHO (40% yield). R. T.

Oxidation of organic compounds with selenium dioxide. VII. Oxidation of substituted acetophenones. N. N. Melnikov and M. S. Rokitzkaja (*J. Gen. Chem. Russ.*, 1940, **10**, 1439—1441).—The velocity of oxidation of C$_6$H$_4$R·COMe by SeO$_2$ in 75% AcOH at 30° rises in the order R = *m*-NO$_2$ < *p*-Br < *p*-Cl < H < *p*-OMe < *p*-Me < *p*-I. That of CH$_2$Ph·COMe is > that of *p*-C$_6$H$_4$I·COMe. R. T.

Dispersion spectra of crystalline and amorphous benzophenone.—See A., 1941, I, 397.

Pinacol–pinacolone rearrangement of phenyl-substituted benzopinacols. H. H. Hatt, A. Pilgrim, and (Miss) E. F. M. Stephenson (*J.C.S.*, 1941, 478—483).—*o*-C$_6$H$_4$Ph·COPh (I) (*anil*, m.p. 91—92°) and Zn–KOH–EtOH at 30° for 5 days afford *o*-*phenylbenzhydrol*, m.p. 71°, which is converted by warm H$_2$SO$_4$–AcOH (3 : 1) into 9-phenylfluorene. With Zn–AcOH at 25—30° for 10 days, or with Na–Et$_2$O in N$_2$, (I) gives s-*di*-*o*-*phenylbenzopinacol* (II), α- (+H$_2$O), m.p. 175° (decomp.), and β-form (+H$_2$O), m.p. 152—160° (boiling CHCl$_3$ converts β into α), also obtained in small yield from MgPhBr, Mg, and *o*-C$_6$H$_4$Ph·CO$_2$Me in N$_2$, but not formed by irradiation of (I) in Pr$^{\beta}$OH. (II) (α or β) and I in 20% NaOAc–AcOH yield (I). *m*-C$_6$H$_4$Ph·MgBr (prepared with active Mg in N$_2$) and PhCN yield m-*phenylbenzophenone*, m.p. 79°, b.p. 264—267°/25 mm. (*benzhydrol*, m.p. 81°), which by photochemical reduction in Pr$^{\beta}$OH affords s-*di*-m-*phenylbenzopinacol* (III), m.p. 178°, in 55% yield (20% yield by Zn–AcOH). Migratory aptitudes in the pinacol–pinacolone rearrangement are found to be *p*-, 3·7, and *m*-C$_6$H$_4$Ph, 0·4 (Ph = 1; *o*-C$_6$H$_4$Ph = 0), which agrees with the order suggested by Burton *et al.* (A., 1929, 1052), viz., α-C$_{10}$H$_7$ > β-C$_{10}$H$_7$ > *p*-C$_6$H$_4$Ph > *m*-C$_6$H$_5$Ph, in connexion with the stability of CAr$_3$. A comparison of agents [2% HClO$_4$ in anhyd. AcOH (3·75) or in AcOH + 4% H$_2$O (2·6); HI–AcOH (3·75); *p*-C$_6$H$_4$Me·SO$_3$H–AcOH (3·9)] used with *s*-di-*p*-phenylbenzopinacol (IV), m.p. 198—201°, as substrate shows that the extent of migration of *p*-C$_6$H$_4$Ph (aptitude quoted) and Ph is independent of the agent, except in case of AcCl–AcOH–C$_6$H$_6$, which suggests increased migration of Ph. The migratory aptitude of *p*-C$_6$H$_4$Ph as obtained by Gomberg *et al.* (A., 1927, 245) is not confirmed. Wide differences in vals. for migratory aptitudes with various reagents are encountered with (II); agents other than HClO$_4$ bring about the pinacolone change so slowly that side reactions entirely supervene. (II)–HI–AcOH yield (I), whilst (II)–*p*-C$_6$H$_4$Me·SO$_3$H–AcOH give 9-phenylfluorene. Rearrangement of (II) with HClO$_4$ affords solely *o*-*phenylbenzoyldiphenyl*-*o*-*diphenylylmethane* (V), m.p. 195·5°, which is unchanged by boiling 10% KOH–MeOH or –EtOH for 300 hr. Fission to methanes and mixed benzoic acids of (V) is carried out with KOH + a little *iso*-C$_5$H$_{11}$·OH, or better with KOH–NaOH (1 : 1) at 185—195°, and of (III) and (IV), after rearrangement, with KOH–NaOH (1 : 1) or KOH–MeOH. (V) gives some *o*-*phenyltriphenylmethane*, m.p. 138°. Fission of pure *o*-, *m*-, or *p*-C$_6$H$_4$Ph·COPh is carried out by KOH–NaOH (1 : 1) and cleavage figures are given. A. T. P.

Synthesis of substances related to sterols. XXXV. Furfurylideneacetone as a reagent for the extension of ring systems. L. E. King and (Sir) R. Robinson (*J.C.S.*, 1941, 465—470).—2-Methyl*cyclo*pentanone, anhyd. HCN, and a little aq. KCN at 0° afford the cyanohydrin, converted by SOCl$_2$–C$_5$H$_5$N at 100° (bath) into 1-*cyano*-2-*methyl*-Δ^2-cyclo*pentene*, b.p. 68—70°/14 mm., hydrolysed by aq. KOH fo the 1-*carboxylic acid*, m.p. 125°. The corresponding Ba salt with (HCO$_2$)$_2$Ba and sand at 150—200°/2 mm. yields 2-methyl-Δ^1-*cyclo*pentene-1-aldehyde, b.p. 70—75°/14 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 200°), which polymerises when kept. *cyclo*Pentanone, CH(OEt)$_3$, and NaOEt in Et$_2$O afford 2-ethoxymethylene*cyclo*pentanone, b.p. 115—122°/11 mm. (*semiearbazone*, m.p. 222—223°), which with MgMeI–Et$_2$O gives (probably) 2-*methyl*-1-*ethylidene*-Δ^2-cyclo*pentene*, b.p. 96—98°/11 mm. (no adduct with maleic anhydride in C$_6$H$_6$). 2-Methyl*cyclo*pentanone and NaNH$_2$–Et$_2$O, followed by CH$_2$Cl·CO$_2$Et, afford *Et* 2-*methyl*cyclo*pentanone*-2-*acetate*, b.p. 130—133°/14 mm., purified by conversion with Et$_2$C$_2$O$_4$ and Na in light petroleum (3 days) into an oil, which loses CO at 180°/18 mm. to give *Et* 5-*carbethoxy*-2-*methyl*cyclo*pentanone*-2-*acetate*, b.p. 142—146°/0·5 mm., which is subsequently hydrolysed (conc. HCl) and esterified. *cis*-8-Methyl-6-hydrindanone and Br–AcOH–HBr afford a bromoketone (I), which with boiling dry C$_5$H$_5$N or quinoline gives an oily, saturated product from which a *semicarbazone*, m.p. 199°, is obtained. (I) and NMe$_3$–EtOH at 100° yield a quaternary bromide, m.p. 240°, converted by Ag$_2$O–90% EtOH into an oil, b.p. 112—118°/12 mm. (*semicarbazone*, m.p. 200°). *cis*-5-Hydrindanol and PBr$_3$ at <0° give 5-bromohydrindane, b.p. 104—105°/15 mm., which with boiling 20% KOH–EtOH gives a

mixture, b.p. 175—177°/750 mm., of Δ^4- and Δ^5-tetrahydrohydrindenes, oxidised by $KMnO_4$–aq. KOH at 40° to two acids, m.p. 173° and 101° (cf. Hückel *et al.*, A., 1935, 208). Hydrogenation ($SrCO_3$–Pd–MeOH) of 1-keto-7-methoxy-2-methyl-1 : 2 : 3 : 4 : 9 : 10-hexahydrophenanthrene affords a hydrophenanthrol, converted by $Al(OBu^{\gamma})_3$–$COMe_2$–C_6H_6 into 1-keto-7-methoxy-2-methyl-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (**II**), m.p. 118—119° (through hydrolysis of mixed semicarbazones), which with Mg Δ^{γ}-butenyl bromide (method : Hibbit *et al.*, A., 1936, 713) yields a product cyclised by H_2SO_4–Ac_2O–AcOH to an acetate, hydrolysed by KOH–EtOH to 5-*hydroxy*-14-*methoxy*-3-*methyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 18-*dodecahydrochrysene*, m.p. 161—168° (*p*-nitrobenzoate, m.p. 239°). The Na derivative (prep. by $NaNH_2$ in Et_2O) of 2-methyl*cyclo*hexanone with furfurylideneacetone (**III**) in Et_2O gives 2-*keto*-4-*furyl*-10-*methyl*-$\Delta^{1:9}$-*octahydronaphthalene*, b.p. 160—170°/0·05 mm., hydrogenated (Pd–$SrCO_3$–MeOH) to 2-keto-4-furyl-10-methyldecahydronaphthalene, the *semicarbazone*, m.p. 126°, of which with NaOEt–EtOH at 180° yields 1-*furyl*-9-*methyldecahydronaphthalene* (**IV**), b.p. 122—124°/0·4 mm., and a non-ketonic oil, b.p. 155—160°/0·4 mm. (**IV**) and HCl (*d* 1·16)–EtOH, followed by HCl–aq. AcOH, give an oil, oxidised by $KMnO_4$–$COMe_2$ to 9-*methyldecahydronaphthalene*-1-*carboxylic acid*, m.p. 164°. (**II**) and $NaNH_2$–Et_2O (in N_2) followed by (**III**) in Et_2O afford 6-*keto*-14-*methoxy*-4-*furyl*-3-*methyl*-1 : 2 : 3 : 4 : 5 : 6 : 9 : 10 : 11 : 18-*decahydrochrysene*, m.p. 172°. Et β-2-methoxy-6-naphthoylpropionate gives no new products in attempted Reformatsky reactions with Et α-bromo-propionate and -succinate. A. T. P.

Production of *cis*-androsterone.—See B., 1941, III, 269.

Hydroxyquinones. III. Constitution and synthesis of rapanone, the anthelmintic principle of *Rapanea Maximowiczii*, Koidz. M. Asano and K. Yamaguti (*J. Pharm. Soc. Japan*, 1940, **60**, 237—242).—Rapanone (**I**), m.p. 139—140°, is converted by BzCl and C_5H_5N into the *dibenzoate* (**II**), m.p. 88—90°, and by Zn powder and boiling Ac_2O into the *leucotetra-acetate* (**III**), m.p. 117—118°. (**I**) is decomposed by boiling 5% NaOH in H_2 into *α-ketopalmitic acid*, m.p. 65—66° (*oxime*, m.p. 81—82°), oxidised by alkaline H_2O_2 to *n*-pentadecoic acid (**IV**), identified as the *p*-toluidide, m.p. 92—93°. The synthesis of (**IV**) from Et myristate is described. Oxidation ($KMnO_4$–KOH) of (**I**) gives myristic acid, m.p. 51° (*p*-toluidide, m.p. 90—91°). 3 : 4 : 5 : 1-$(OMe)_3C_6H_2$·CO·CH_2·CO_2Et, *n*-$C_{12}H_{25}I$, and NaOEt in boiling EtOH give *Et α*-3 : 4 : 5-*trimethoxybenzoylmyristate*, m.p. 54°, hydrolysed by boiling 1% KOH–EtOH to 3 : 4 : 5-*trimethoxymyristophenone*, m.p. 69°. This is converted by Na and boiling *iso*-C_5H_{11}·OH into 3 : 5-*dimethoxytetradecylbenzene*, b.p. 178°/0·02 mm., m.p. 43°, oxidised ($Na_2Cr_2O_7$, AcOH) to 6-*methoxy*-2-*tetradecyl*-p-*benzoquinone*, m.p. 81—82°, which with EtOH–NH_2Me and subsequent aëration yields 3 : 6-*di*(*methylamino*)-2-*tetradecyl*-p-*benzoquinone* (**V**), m.p. 143°. Acid hydrolysis of (**V**) affords 3 : 6-*dihydroxy*-2-*tetradecyl*-p-*benzoquinone* (**VI**), m.p. 139—140° [*dibenzoate* (**VII**), m.p. 94—95°; *leucotetra-acetate* (**VIII**), m.p. 121·5°]. The m.p. of (**I**) and (**II**) is not depressed by (**VI**) and (**VII**), respectively, whereas (**VIII**) causes a small but definite depression of the m.p. of (**III**). A similar series of changes gives successively *Et α*-3 : 4 : 5-*trimethoxybenzoyltridecoate*, m.p. 49—50°, 3 : 4 : 5-*trimethoxytridecophenone*, m.p. 61—62°, 3 : 5-*dimethoxytridecylbenzene*, m.p. 41·5—42·5°, 6-*methoxy*-, m.p. 82—83·5°, 3 : 6-*di*(*methylamino*)-, m.p. 141—142°, and 3 : 6-*dihydroxy*-2-*tridecyl*-p-*benzoquinone* (**IX**), m.p. 139—140° [*dibenzoate* (**X**), m.p. 91°; *leucotetra-acetate* (**XI**), m.p. 118°]. Since (**IX**), (**X**), and (**XI**) do not depress the m.p. of (**I**), (**II**), and (**III**), respectively, the identity of (**I**) and (**IX**) is regarded as established. H. W.

Hydroxyquinones. IV. Synthesis of dihydroxy-2-alkyl-*p*-benzoquinones. M. Asano and Z. Hase (*J. Pharm. Soc. Japan*, 1941, **61**, 1—6).—*Quinol di*-n-*dodecate* (prep. from quinol, $C_{11}H_{23}$·CO_2H, and $ZnCl_2$ at 140—165°), m.p. 83°, and CH_2N_2 give p-*dodecoxyanisole*, m.p. 32—33°. *n*-$C_{11}H_{23}$·COCl, *p*-$C_6H_4(OMe)_2$, and $AlCl_3$ in CS_2, first at room temp. and later at (?) >100°, give 2-n-*dodecoylquinol* 4-*Me ether* (**I**), m.p. 42—43° (2 : 4-*dinitrophenylhydrazone*, m.p. 121—124°), and 2-n-*dodecoylquinol*, m.p. 99° [with CH_2N_2 gives (**I**)]. Zn–Hg–HCl reduces (**I**) to 2-n-*dodecylquinol* 4-*Me ether*, m.p. 54—56°, b.p. 165—168°/0·3 mm., converted by $AlCl_3$ in hot C_6H_6 into 2-*n*-dodecylquinol, m.p. 109—111°, which with boiling aq. $FeCl_3$ gives 2-*n*-dodecoyl-*p*-benzoquinone, m.p. 74° (lit. 81°). With NH_2Me–EtOH this gives 1 : 3 : 6 : 2 : 4-O:$C_6H(NHMe)_2(C_{12}H_{25}$-*n*):O, m.p. 146—148°, hydrolysed by H_2SO_4–AcOH to 1 : 3 : 6 : 2 : 4-O:$C_6H(OH)_2(C_{12}H_{25}$-*n*):O (structure proved by oxidation by H_2O_2 to *n*-$C_{12}H_{25}$·CO_2H). Similarly are prepared : 2-n-*undecoyl*-, m.p. 73·5—74·5° [4-*Me ether*, m.p. 47·5—48·5° (2 : 4-*dinitrophenylhydrazone*, m.p. 125—127°); *dibenzoate*, m.p. 93—94·5°], 2-n-*tetradecoyl*-, m.p. 101—103° (4-*Me ether*, m.p. 51—52°), 2-n-*hexadecoyl*-, m.p. 103—104° (4-*Me ether*, m.p. 59—60·5°), 2-n-*octadecoyl*-, m.p. 106—108·5° (4-*Me ether*, m.p. 63—64°), 2-n-*undecyl*-, m.p. 100—101·5° (4-*Me ether*, m.p. 51—52·5°, b.p. 162°/0·5 mm.), 2-n-*tetradecyl*-, m.p. 110—112° (4-*Me ether*, m.p. 57—60°, b.p. 195°/0·15 mm.), 2-n-*hexadecyl*-, m.p. 110—111°, and 2-n-*octadecyl*-, m.p. 112—114° (4-*Me ether*, m.p. 73—75, b.p. 226—228°/0·8 mm.), *-quinol*; 2-n-*undecyl*-, m.p. 57—59°, 2-n-*tetradecyl*-, m.p. 78—79°, 2-n-*hexadecyl*-, m.p. 82—83°, and 2-n-*octadecyl*-, m.p. 84—85°, -p-*benzoquinone*; 3 : 6-*di*(*methylamino*)-2-*n*-undecyl-, m.p. 145—148° (with H_2SO_4–AcOH gives embelin), -2-n-*hexadecyl*-, m.p. 140°, and -2-n-*octadecyl*-, m.p. 138—140°, -p-*benzoquinone*; 3 : 6-*dihydroxy*-2-n-*hexadecyl*-, m.p. 132—134° (*dibenzoate*, m.p. 93—95°), and -2-n-*octadecyl*-p-*benzoquinone*, m.p. 134—135° (*dibenzoate*, m.p. 92—93°). Reduction of the $(OH)_2$-quinone by Zn dust, Ac_2O, and a drop of H_2O at 100° and later, when cold, a little conc. H_2SO_4 gives 2 : 3 : 5 : 6-*tetra-acetoxy*-n-*hexa*-, m.p. 117—119°, and *-octa-decylbenzene*, m.p. 119·5—120·5°. R. S. C.

Hydroxyquinones. VI. Synthesis of dihydroxydialkylbenzoquinones. M. Asano and H. Takahashi (*J. Pharm. Soc. Japan*, 1941, **61**, 65—66).—$Et_2C_2O_4$, CH_2R·CO_2Et (R = *iso*-C_5H_{11}, *n*-C_7H_{15}, *n*-$C_{10}H_{21}$), and Na in Et_2O afford small amounts only of 3 : 6-*dihydroxy*-2 : 5-*di*isoa*myl*-, m.p. 177—178° (*dibenzoate*, m.p. 170°), *-di*-n-*heptyl*-, m.p. 143° (*dibenzoate*, m.p. 100°), and *-di*-n-*decyl*-*benzoquinone*, m.p. 131—132° (*di-benzoate*, m.p. 87°), and thence (Zn–Ac_2O + H_2O) 2 : 3 : 5 : 6-*tetra-acetoxy*-1 : 4-*di*isoa*myl*-, m.p. 162°, *-di*-n-*heptyl*-, m.p. 107°, and *-di*-n-*decyl*-*benzene*, m.p. 112°, respectively. A. T. P.

Peroxidase action. III. Oxidation of mesidine. N. B. Chapman and B. C. Saunders (*J.C.S.*, 1941, 496—500; cf. A., 1940, II, 283).—The system dil. aq. H_2O_2 (added gradually) and peroxidase oxidises mesidine (**I**) (2% solution) at room temp. and p_H 4·0—4·7 (dil. AcOH), when 2 : 6-*dimethyl*-p-*benzoquinone*-4-(2′ : 4′ : 6′-*trimethyl*)*anil* (**II**), m.p. 97°, separates gradually; a purified enzyme prep. gives 95% yield. Formation of (**II**) thus involves loss of Me, and the mechanism of reaction of discussed. (**I**) and H_2O_2–$FeSO_4$–dil. AcOH yield an amorphous product containing only traces of (**II**). (**I**)–PbO_2–AcOH–Et_2O afford (chromatographic analysis) azomesitylene, m.p. 75°. (**II**) with Zn dust in boiling Ac_2O–C_5H_5N gives the ON-*Ac*$_2$ derivative, m.p. 143°, of 4-hydroxy-2 : 6 : 2′ : 4′ : 6′-pentamethyldiphenylamine; hydrolysis (boiling 10% H_2SO_4) of (**II**) yields (**I**) and 1 : 2 : 6 : 4-O:$C_6H_2Me_2$:O (**III**), whilst (**I**) and (**III**), alone or in aq. AcOH (+a trace of $COMe_2$), give (**II**). (**I**) does not condense with 5-nitroso-*m*-2-xylenol. Oxidation ($K_2Cr_2O_7$–aq. NaOH at room temp.) of (**I**) gives (**II**) (8%), but equimol. mixtures of (**I**) with *m*-2- or *m*-5-xylenol afford 26 or 0—1%, respectively, of (**II**). A. T. P.

Phenol amidine reaction : detection of guanidine, guanidine derivatives, and carbamide by thymol and hypochlorite. W. R. Fearon (*Sci. Proc. Roy. Dublin Soc.*, 1941, **22**, 415—421; cf. Sakaguchi, *J. Biochem. Japan*, 1925, **5**, 13, 23).—At p_H 8·5—10, $CO(NH_2)_2$, $NH:C(NH_2)_2$, and NH_2·C(NH)·NHR (free or in protein form) with thymol (or a phenol containing H *para* to OH) and NaOCl give stable yellow quinonoid pigments probably of the type *p*-O:C_6H_4:N·C(NH)·NR·C_6H_3·OH-*p*. At p_H >11 only substituted guanidines react. The conditions and mechanism of this and the indophenol reaction are discussed. A. Li.

Hydroxyquinones. V. Synthesis of phthiocol, pigment of the tubercle bacillus. M. Asano and Z. Hase (*J. Pharm. Soc. Japan*, 1941, **61**, 55—57).—2-Methyl-1 : 4-naphthaquinone and NH_2Me–EtOH at room temp., aërated for 1 hr., yield 3-*methylamino*-, m.p. 127—129°, and thence (50% H_2SO_4–AcOH) 3-hydroxy-2-methyl-1 : 4-naphthaquinone (**I**) (phthiocol), m.p. 171—172° (*benzoate*, m.p. 129—130·5°; Ac_2O–Zn–NaOAc afford 1 : 2 : 4-*triacetoxy*-3-*methylnaphthalene*, m.p. 155·5—156°). *Et butyrophenone*-o-*carboxylate*, b.p. 160—163°/11 mm., and *iso*amyl nitrite in HCl–Et_2O give *α-oximino-butyrophenone*-o-*carboxylic acid* (**II**), m.p. 157° (decomp.), and

some 2 : 5-*di*-(*o*-*carboxyphenyl*)-3 : 6-*dimethyl*-1 : 4-*benzoquinonedioxime*, m.p. 273—274° (decomp.). (**II**) and aq. H_2SO_4 at 100° (bath) give *o*-*carboxyphenyl Et diketone*, m.p. 88—90°, the *Et* ester, b.p. 130°/3 mm., of which with NaOEt–Et_2O then affords (**I**). A. T. P.

III.—TERPENES.

Distribution of the double linkings in irone. A. E. Gillam and T. F. West (*Nature*, 1941, **148**, 114).—Irone shows an intense absorption band at 2280 A., and an inflexion near 3080 A., the two together being characteristic of a $\alpha\beta$-unsaturated ketone. The location of the intense band indicates the presence of a monosubstituted $\alpha\beta$-unsaturated ketone, probably CHR:CH·COR, and shows that the C:C·C:C·C:O structure is absent. The similarity between the absorption spectra of α-ionone (λ max. 2285 A.) and irone (λ max. 2280 A.) supports this view. L. S. T.

Catalytic transformations of terpenes. I. Action of activated clay on dipentene. G. A. Rudakov (*J. Gen. Chem. Russ.*, 1940, **10**, 1673—1681).—Dipentene is converted into terpinolene, and this in turn into α-terpinene, by boiling under reflux with fireclay treated with HCl. *p*-Cymene, Δ^3-*p*-menthene, and polyterpenes are also formed as secondary products, and, as these are more stable than are the primary ones, they alone survive prolonged treatment. R. T.

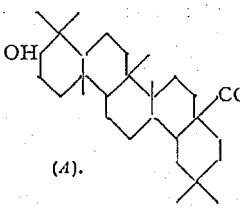
Halogen derivatives of fenchone, and their transformations. L. J. Briusova (*J. Gen. Chem. Russ.*, 1940, **10**, 1462—1470).—Chlorination of fenchone at 60—70° (Cu catalyst) yields *chlorofenchone*, b.p. 113—117°/12 mm. Bromofenchone, as obtained by Czerny (A., 1900, i, 675), is a mixture of products, including bromocamphor, 6-bromofenchone, and probably bromo*iso*fenchone. The mixture is converted by NaOEt in EtOH into a mixture of alcohols, of which borneol, probably *iso*fenchyl alcohol, and possibly fenchyl alcohol were identified. Reduction with Na in EtOH of the polybromide fraction of the bromination product gave an *alcohol*, $C_{10}H_{17}$·OH, b.p. 88·4—89°/13 mm. (*H phthalate*, m.p. 101—103°; *acetate*, b.p. 88—89°/10 mm.), oxidised by HNO_3 to fenchone. R. T.

***iso*Fenchone. II. *iso*Fenchoquinone and its derivatives, and hydroxy*iso*fenchones.** A. K. Rushentzeva and N. M. Delektorskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 1653—1656; cf. A., 1941, II, 172).—*iso*Fenchone and SeO_2 in Ac_2O (5 hr. at 140—150°) yield *iso*fenchoquinone, m.p. 69—70° (lit., m.p. 49—50°) (*semicarbazone*, m.p. 165—166°; *phenylhydrazone*, m.p. 125—126°; *oxime*, m.p. 138·5—139·4°), reduced by Zn in AcOH to *hydroxy*iso*fenchoquinone*, obtained in two isomeric forms, m.p. 50—53° and 114—115°. R. T.

Order of reactions of hydrogenation and dehydrogenation.—See A., 1941, I, 421.

Triterpenes from Japanese *Skimmia* species. I. Skimmiol and skimmione. K. Takeda (*J. Pharm. Soc. Japan*, 1941, **61**, 63—65).—Extraction of the leaves of *Skimmia Japonica*, Thunb., and *S. repens*, Nakai (cf. Asahina, A., 1930, 1454), gives a neutral portion, m.p. 236—238°, which affords (chromatographic analysis) *skimmiol* (**I**), $C_{30}H_{50}O$, m.p. 279—281°, $[\alpha]_D^{19}$ +3·1° in $CHCl_3$ [*mono-acetate* (**II**), m.p. 298—299°, $[\alpha]_D^{23}$ +13·8° in $CHCl_3$, *-benzoate*, m.p. 287—289°, $[\alpha]_D^{21}$ +35·5° in $CHCl_3$, and *-formate*, m.p. 267—269°], and *skimmione* (**III**), $C_{30}H_{48}O$, m.p. 241—243°, $[\alpha]_D^{23}$ +12·2° in $CHCl_3$ [*mono-oxime*, m.p. 292—294°; *oxime acetate*, m.p. 224—225° (decomp.); *dibromide*, m.p. 211° (decomp.)], reduced (Clemmensen) to *skimmiene*, $C_{30}H_{50}$, m.p. 188—190°, $[\alpha]_D^{21}$ −20·5° in $CHCl_3$. (**I**) is oxidised by CrO_3 to (**III**). Catalytic hydrogenation of (**III**), followed by acetylation, affords (**II**). (**III**) is reduced by Na and *iso*-C_5H_{11}·OH to (**I**) and iso*skimmiol* (chromatographic separation), m.p. 267—269°. $[\alpha]_D^{22}$ +11·9° in $CHCl_3$ (*acetate*, m.p. 205—207°, $[\alpha]_D^{16}$ −31·8° in $CHCl_3$; *benzoate*, m.p. 274—275°, $[\alpha]_D^{13}$ −25·2° in $CHCl_3$). A. T. P.

Saponins. XVI. Constitution of nitro-compounds of the oleanolic acid series. II, III. S. Kuwada and K. Takeda (*J. Pharm. Soc. Japan*, 1940, **60**, 157—160, 249—250; cf. A., 1940, II, 221).—II. Nitration of acetyloleanolic acid (**I**) with fuming HNO_3 in AcOH and methylation (CH_2N_2) of the product affords *Me nitroacetyloleanolate* (**II**), decomp. 228°, $[\alpha]_D^{18}$ +98·5°. This when boiled with Zn dust and AcOH is converted into a neutral product separated by MeOH into ketoacetyloleanolactone (**III**) decomp. 317°, $[\alpha]_D^{24}$ +116·5°, *Me* iso*ketoacetyldihydro-oleanolate* (**IV**), m.p. 261—263°, $[\alpha]_D^{21}$ +6·4°, and Me ketoacetyldihydro-oleanolate (**V**), m.p. 198—199°, $[\alpha]_D^{24}$ −12·0°. (**III**) does not contain OMe, does not give an oxime or semicarbazone, has an absorption max. at 273 mμ., and is hydrolysed exclusively to keto-oleanolactone (**VI**), decomp. 322°, $[\alpha]_D^{24}$ +118·4°. (**IV**) contains 1 OMe, and has an absorption max. at 264 mμ.; on hydrolysis it affords solely *Me* iso*ketodihydro-oleanolate*, m.p. 220—221°. The absorption curve of (**V**) has a max. at 286 mμ. The Röntgen spectra of (**IV**) and (**V**) are distinct so that (**IV**) and (**V**) must be regarded as isomerides. Hydrolysis of (**V**) gives Me ketodihydro-oleanolate, m.p. 202—203°. Oxidation (CrO_3) of (**VI**) gives *keto-oleanonolactone*, m.p. 276—279°, $[\alpha]_D^{22}$ +155° (*oxime*, decomp. 276—277°; absorption max. at 272 mμ.). The changes recorded are in harmony with the constitution (*A*) for oleanolic acid. M.p. etc. are corr. and [α] are in $CHCl_3$.



(*A*).

III. Fuming HNO_3 in AcOH converts (**I**) into *nitroacetyloleanolic acid* (**VII**), decomp. 221—222°, $[\alpha]_D^{23}$ +95·5° in $CHCl_3$, hydrolysed by 5% KOH–MeOH to *nitro-oleanolic acid*, decomp. 229—230°, and methylated by CH_2N_2 to (**II**). (**VII**) is transformed by Zn dust and AcOH into neutral and acid products. The former are separated by MeOH into α- (**VIII**), decomp. 314°, and *β-ketoacetyloleanololactone* (**IX**), decomp. 286—288°, $[\alpha]_D^{17}$ +9·4° in $CHCl_3$. (**VIII**) and (**IX**) are distinguished from one another by the Röntgen diagrams. Under the influence of 10% KOH–MeOH (**VIII**) only loses Ac whereas (**IX**) is converted into *ketohydroxydihydro-oleanolic acid*, decomp. 304°. Probably (**VIII**) is a γ- and (**IX**) is a δ-lactone. The physical properties and certain derivatives of the so-called "ketoacetyl-lactone" obtained by oxidising (**I**) with CrO_3 agree completely with those of (**IX**). The acidic product is ketoacetyldihydro-oleanolic acid. H. W.

Position of the carboxyl group in oleanolic and related acids. P. Bilham and G. A. R. Kon (*Nature*, 1941, **147**, 745).—Evidence that the CO_2H is in one of the terminal rings is discussed. L. S. T.

Constituents of the branches of *Akebia quinata*, Decne. R. Kawaguchi and K. W. Kim (*J. Pharm. Soc. Japan*, 1940, **60**, 236).—"Akebigenin," obtained by hydrolysis of akebin; is a mixture of hederagenin and oleanolic acid. H. W.

Constituents of "senso." XI. Constitution of acetyl-ψ-deacetylbufotalin. S. Ohno (*J. Pharm. Soc. Japan*, 1940, **60**, 226—230; cf. A., 1939, II, 382, 438).—Acetyl-ψ-deacetylbufotalin (**I**) is oxidised by $KMnO_4$ to *ψ-ætiocholanic acid*, m.p. 180—183°, which does not give a cryst. phenacyl ester. The presence of a *tert.* OH at $C_{(14)}$ in it is established by the production of a lactone under the influence of HCl–EtOH. In the sterol nucleus of (**I**) there remains OH which cannot be acylated. To elucidate its nature the nuclear C_{17} ketone (*loc. cit.*) is oxidised by KOBr in alkaline solution, whereby little acid is produced and the sterol nucleus appears to be altered, by SeO_2 in AcOH, whereby an *o*-diketone is formed in small amount, and by CrO_3 in warm AcOH, giving a neutral substance, $C_{18}H_{28}O_4$, sol. in warm 2% $NaHCO_3$, and a dicarboxylic acid which readily loses CO_2 to yield a monocarboxylic acid. This partial decarboxylation is completed and lactonisation occurs during distillation in a high vac. The *lactone* (**II**) in C_5H_5N affords a p-*nitrobenzoate*, so that OH at $C_{(3)}$ is not involved in lactone formation and the *tert.* OH at β-$C_{(14)}$ is certainly not adapted thereto. Probably the active OH is at $C_{(9)}$ and *trans* to OH at $C_{(14)}$. This is shown by conversion of (**II**) by AcOH–HBr followed successively by 20% KOAc–EtOH and Ac_2O into a *deoxyacetyllactone*, $C_{18}H_{26}O_3$·C_2H_2O, which immediately decolorises $KMnO_4$. This is ozonised in $CHCl_3$ to a little of a neutral substance, an acid (**III**) which gives an orange-red colour with $FeCl_3$, but no $H_2C_2O_4$. (**III**) gives a distinct diazo-reaction, and yields a non-cryst. Me ester and a *semicarbazone*, $C_{21}H_{32}O_6$·CH_3ON_3, m.p. >280°, which does not give the diazo-change. (**III**) is therefore a β-CO-acid. It follows therefore that a *tert.* non-acylable OH is at $C_{(9)}$ and forms a link of the β-CO-lactone. Formulæ are suggested. H. W.

Constituents of *Zyzyphus vulgaris*, Lamark, var. *spinosus*, Bunge. II. Betulic acid. R. Kawaguchi and K. W. Kim (*J. Pharm. Soc. Japan*, 1940, **60**, 235—236).—Betulonic acid,

m.p. 253°, obtained by the oxidation of betulic acid, gives a *semicarbazone*, m.p. 282—283°. It is reduced catalytically to *dihydrobetulonic acid*, m.p. 256—257°, shown by comparison of its *semicarbazone*, m.p. 284—285°, to be identical with the acid obtained by oxidation of dihydrobetulin and dihydrobetulic acid. H. W.

Substitution reactions of dehydroabietic acid. II. W. P. Campbell and M. Morgana (*J. Amer. Chem. Soc.*, 1941, **63**, 1838—1843; cf. A., 1939, II, 30).—6-Sulphodehydroabietic acid (**I**) (modified prep.; 78% yield; cf. *loc. cit.*), $+3H_2O$, m.p. (immediate) 215° (evolution of H_2O), resolidifies, decomp. 227°, and Br or Br–NaBr in H_2O at 100° give 92% of 6-*bromodehydroabietic acid* (**II**), m.p. 200—202°, $[\alpha]_D^{25}$ +81° in EtOH (*Me* ester, m.p. 140·5—141°, $[\alpha]_D^{25}$ +71° in $COMe_2$), also obtained (impure acid, pure ester) from dehydroabietic acid by Br–CCl_4 at 60°. The structure of these acids is proved by conversion of (**I**) by 12% aq. NaOH–N_2 at 290° and then CH_2N_2–Et_2O into the known Me 6-hydroxydehydroabietate (27—44%), m.p. 158—161·5°. With conc. aq. NH_3 and CuBr at 200°, (**II**) gives 42% of 6-aminodehydroabictic acid (**III**), m.p. 211—214°, isolated (59%) as cryst. hydrochloride. Me 6 : 8-dinitrodehydroabietate (**IV**) (orientation rendered very probable by reactions given below) and boiling H_2S–NH_3–H_2O–MeOH give 91% of *Me* 8-*nitro*-6-*aminodehydroabietate* (**V**), m.p. 239—242°, $[\alpha]_D^{25}$ +105° in $COMe_2$ (impure hydrochloride, m.p. 247—248·5°; NN-Ac_2 derivative, m.p. 203·5—206°, $[\alpha]_D^{25}$ +97° in $COMe_2$). Reduction of the 6 : 8-$(NO_2)_2$-acid by Na_2S–NH_4Cl–aq. EtOH gives 11% of 8-*nitro*-6-*aminodehydroabietic acid* (**VI**), m.p. 285·5—286° (decomp.), $[\alpha]_D^{25}$ +117° in $COMe_2$ [isolated (22%) as hydrochloride; Me ester = (**V**)]. H_2SO_4–HNO_3 and (**III**) at <0° give a moderate yield of (**VI**) [m.p. 282·5—283° (decomp.); Me ester = (**V**), m.p. 241—243°]. Diazotisation (H_2SO_4–$NaNO_2$–H_3PO_4) of (**V**) and digestion of the diazonium salt in EtOH with or without Zn powder gives 40% of *Me* 8-*nitrodehydroabietate*, m.p. 194—195°, $[\alpha]_D^{25}$ +29° in $COMe_2$, and thence (H_2SO_4–HNO_3; 0°) (**IV**). With H_2SO_4–HNO_3, in yields varying according to the conditions, (**I**) gives 8-nitro-6-dehydroabietic acid (up to 81%) (Me_2 ester, m.p. 243·5—244°; cf. Hasselstrom *et al.*, A., 1941, II, 143) and (by way of 6-nitrodehydroabietic acid) 3—22% of 6 : 8-$(NO_2)_2$-acid. M.p. are corr. [N. B. Eddy] β-Dimethylaminodehydroabietinol Me ether hydrochloride has no analgesic and little toxic effect. R. S. C.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Luminescent oxidation of luciferin. P. N. Chakravorty and R. Ballentine (*J. Amer. Chem. Soc.*, 1941, **63**, 2030—2031).—Purified extracts of *Cypridina* luciferin (**I**) contain only C, H, and O. $CO{\cdot}CH_2{\cdot}OH$ is present. With NH_2OH,AcOH it gives a micro-cryst. ppt., which is inactive towards luciferase (**II**) but is reactivated by acid hydrolysis. Luminescent oxidation involves $R{\cdot}CO{\cdot}CH_2{\cdot}OH \rightarrow$ (**II**) RCO_2H (irreversible). The luminescent activity is restored by the reactions, $RCO_2H \rightarrow$ ($SOCl_2$) $RCOCl \rightarrow$ (CH_2N_2) $RCO{\cdot}CHN_2 \rightarrow$ dil. H_2SO_4) $RCO{\cdot}CH_2{\cdot}OH$. Oxidation of the quinol nucleus is the reversible oxidation of (**I**) by O_2. R. S. C.

Action of organic nitrogen bases on cornstalk lignin. E. Fisher and R. S. Bower (*J. Amer. Chem. Soc.*, 1941, **63**, 1881—1883).—The amounts of cornstalk tissues or the lignin isolated therefrom by 72% H_2SO_4 which is dissolved by aq. or anhyd. mono-, di-, or tri-ethanolamine, morpholine–EtOH, or NEt_3 increase with the strength of the base. Compound formation is probable. R. S. C.

V.—HETEROCYCLIC.

Condensation of furan derivatives. XIII. Displacement of one aldehyde by another from carbonyl-ethylene compounds. V. V. Tschelincev and E. K. Nikitin (*J. Gen. Chem. Russ.*, 1940, **10**, 1453—1456).—The velocities of reaction of $COMe_2$ in aq. KOH with salicylaldehyde, vanillin, PhCHO, and furfuraldehyde are as 0·00125 : 0·00645 : 0·2 : 1. Each member of the series will displace the preceding ones from condensation with $COMe_2$. R. T.

Constitution of the condensation product of furfuraldehyde and aniline (Schiff's base). E. R. Riegel and (Miss) M. Hathaway (*J. Amer. Chem. Soc.*, 1941, **63**, 1835—1838).—The violet substance obtained from furfuraldehyde (**I**), NH_2Ph, and NH_2Ph,HCl (Stenhouse *et al.*, *Annalen*, 1870, **156**, 199) is 2-di-(*p*-aminophenyl)methylfurfuraldehyde monohydrochloride, $+H_2O$ (**II**) (cf. Zincke *et al.*, A., 1906, i, 33), since it is quantitatively tetrazotised in 95% EtOH and then coupled with 9 products to give *dyes*. Similar results are recorded for products from (**I**) and other bases. A mechanism is proposed to account for formation of NH_2Ph and 3-hydroxy-1-phenylpyridinium halide from (**II**) by boiling AcOH or, less well, EtOH. The violet substance obtained (König, A., 1904, i, 449) differs from (**II**) and does not react with HNO_2. R. S. C.

Benzopyrone series. IV. Synthesis of karanjin. T. R. Seshadri and V. Venkateswarlu (*Proc. Indian Acad. Sci.*, 1941, **13**, A, 404—410).—Karanjic acid (**I**) is converted (MeOH–conc. H_2SO_4) into its *Me* ester, m.p. 105—106°, transformed by MeI and anhyd. K_2CO_3 in boiling $COMe_2$ but not by Me_2SO_4–NaOH into *Me* O-*methylkaranjate*, also obtained directly by the prolonged action of K_2CO_3 and MeI on (**I**) in boiling $COMe_2$. It is hydrolysed by 25% aq. NaOH to O-*methylkaranjic acid*, m.p. 148°, which with PCl_5 in CCl_4 gives the *chloride*, m.p. 72°. This is condensed with Et αγ-dimethoxysodioacetoacetate (**II**) in Et_2O and the product is hydrolysed to 4-*methoxy*-5-ω-*methoxyacetylcoumarone*, m.p. 87—88°, which was also obtained by the protracted action in boiling $COMe_2$ of MeI and K_2CO_3 on 4-hydroxy-5-ω-methoxyacetylcoumarone (**III**), obtained in 95% yield by the action of KOH–anhyd. MeOH on karanjin (**IV**); very little (**I**) is produced by this method. Gradual addition of AcCl to (**I**) in well-cooled C_5H_5N leads to *acetylkaranjic acid*; the noncryst. *chloride* is condensed with (**II**) to (**III**), from which (**IV**) is obtained in good yield by the action of Bz_2O and NaOBz at 180°. H. W.

Condensation of α-substituted acetoacetates with phenols. III. Pechmann condensation of ethyl α-(βββ-trichloro-α-hydroxyethyl)acetoacetate. IV. Condensation of cresols and other less reactive phenols with ethyl α-(βββ-trichloro-α-hydroxyethyl)acetoacetate. D. R. Kulkarni, R. L. Alimchandani, and N. M. Shah (*J. Indian Chem. Soc.*, 1941, **18**, 113—119, 123—126).—III. m-$C_6H_4(OH)_2$, 1 : 2 : 3- and 1 : 3 : 5-$C_6H_3(OH)_3$, α-$C_{10}H_7{\cdot}OH$, and 1 : 3 : 5-$C_6H_3Me(OH)_2$ with $CCl_3{\cdot}CH(OH){\cdot}CHAc{\cdot}CO_2Et$ (**I**) and $POCl_3$ give good yields of 7-*hydroxy*-, m.p. 207—208° (decomp.) (**II**) (*Me*$_2$ *ether*, m.p. 154—155°; *Ac*$_2$, m.p. 149—150°, and *Bz* derivative, m.p. 169—170°), 7 : 8- (**III**), m.p. 223° (decomp.) (*Me*$_3$ *ether*, m.p. 139°; *Ac*$_3$ derivative, m.p. 181°), and 5 : 7-*dihydroxy*-, m.p. 216—217°, -4-*methyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin* (*Ac*$_3$ derivative, m.p. 147—148°), 4-*methyl*-3-βββ-*trichloro*-α-*hydroxyethyl*-1 : 2-α-*naphthapyrone*, m.p. 231—232° (*Ac* derivative, m.p. 207—208°), and 5-*hydroxy*-4 : 7-*dimethyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin*, m.p. 223—224° (decomp.), respectively. (**II**) and (**III**) are reduced (Zn + AcOH) to 7-*mono*-, m.p. 254—255° (decomp.) *Ac* derivative, m.p. 169—170°), and 7 : 8-*di*-*hydroxy*-4-*methyl*-3-β-*chlorovinylcoumarin*, m.p. 231—232° (decomp.), which with Me_2SO_4 and aq. KOH in $COMe_2$ at 100° yield 2 : 4-*di*-, m.p. 172—173° (*Ag* salt), and 2 : 3 : 4-*tri*-*methoxy*-β-*methyl*-α-(β-*chlorovinyl*)*cinnamic acid*, m.p. 125—126° (*Ag* salt). With H_2SO_4 or P_2O_5 as catalyst, m-$C_6H_4(OH)_2$ and 1 : 3 : 5-$C_6H_3(OH)_3$ condense with (**I**) as above, but α-$C_{10}H_7{\cdot}OH$ does not condense. 1 : 2 : 3-$C_6H_3(OH)_3$ and 1 : 3 : 5-$C_6H_3Me(OH)_2$ with P_2O_5 do not condense, and with H_2SO_4 give uncrystallisable products. $AlCl_3$ is unsatisfactory.

IV. PhOH, α-$C_{10}H_7{\cdot}OH$, *p*-$C_6H_4(OH)_2$, and 1 : 2 : 4-$COMe{\cdot}C_6H_3(OH)_2$ give no cryst. products with (**I**). (**I**) with *p*-cresol and H_2SO_4 at <0° yields 4 : 6-*dimethyl*-3-βββ-*trichloro*-α-*hydroxyethylcoumarin*, m.p. 202—203° (*Me ether*, m.p. 207°). (**I**) and *o*- and *m*-cresol in cold EtOH with H_2SO_4 yield γγγ-*trichloro*-β-4-*hydroxy*-3-, m.p. 186—187° (*Ac* derivative, m.p. 75°; *semicarbazone*, m.p. 256—257°), and -2-*methylphenylpropyl Me ketone*, m.p. 208—209° (decomp.) (*Ac* derivative, m.p. 104—105°; *semicarbazone*, m.p. 214°). A. Li.

Colouring matters of the flavone series. VI. Constituents of *Zinnia elegans* (Jacq.); synthesis of apigenin glucoside. T. Nakaoki (*J. Pharm. Soc. Japan*, 1940, **60**, 190—191; cf. A., 1939, II, 441).—The flowers yield apigenin glucoside (~1%), m.p. 226—227° (from aq. C_5H_5N) (5 : 7 : 4′-trihydr-

oxyflavone-7-glucoside), identical with that obtained by synthesis through apigeninglucose tetra-acetate. A. T. P.

Synthesis of nobiletin (5 : 6 : 7 : 8 : 3′ : 4′-hexamethoxyflavone). Z. Horii (*J. Pharm. Soc. Japan*, 1940, **60**, 246—248).—2-Hydroxy- is oxidised by $K_2S_2O_8$ and NaOH to 2 : 5-*dihydroxy*-3 : 4 : 6-*trimethoxyacetophenone*, m.p. 125—126°, partly methylated (Me_2SO_4 and K_2CO_3 in $COMe_2$ at 50°) to 2-*hydroxy*-3 : 4 : 5 : 6-*tetramethoxyacetophenone*, b.p. 148°/7 mm., which with veratroyl chloride and C_5H_5N at 100° affords the *veratroyl* derivative, m.p. 118·5—119·5°. This is isomerised by $NaNH_2$ in PhMe at 100° to 2-*hydroxy*-3 : 4 : 5 : 6-*tetramethoxy*-ω-*veratroylacetophenone*, m.p. 113·5—114·5°, converted by NaOAc and glacial AcOH at 100° or by conc. H_2SO_4 at 0° into 5 : 6 : 7 : 8 : 3′ : 4′-hexamethoxyflavone (**I**), m.p. 136·5—137·5°, identical with nobiletin. (**I**) is transformed by boiling 30% HCl into 5-hydroxy-6 : 7 : 8 : 3′ : 4′-pentamethoxyflavone, m.p. 144—145°. It is demethylated by HI (*d* 1·7) at 140° and then converted by Ac_2O and C_5H_5N into hexa-acetoxy-, m.p. 230·5—231·5°, and by BzCl and C_5H_5N at 100° into hexabenzoyloxy-flavone, m.p. 244—245°. H. W.

Tetrahydrocannabinol homologues with marihuana activity. IX. R. Adams, S. Loewe, C. Jelinek, and H. Wolff. **X.** R. Adams, C. M. Smith, and S. Loewe. **XI.** R. Adams, C. K. Cain, and S. Loewe (*J. Amer. Chem. Soc.*, 1941, **63**, 1971—1973, 1973—1976, 1977—1978; cf. A., 1940, II, 379).—Relative marihuana potencies are denoted *P* below relative to the *n*-amyl derivative. M.p. are corr. IX. 5 : 1 : 3-$C_6H_3R(OH)_2$, Et 5-methyl*cyclo*hexanone-2-carboxylate (**I**) and $POCl_3$ in C_6H_6 give 6″-*hydroxy*-5′-*methyl*-4″-n-*propyl*-, m.p. 233—235°, -n-*butyl*-, m.p. 199—200°, -n-*hexyl*-, m.p. 173—174°, -n-*heptyl*-, m.p. 172—173°, and -n-*octyl*-, m.p. 165—167°, -3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyrone*, converted by MgMeI into 6″-*hydroxy*-2 : 2 : 5′-*trimethyl*-4″-n-*propyl*-, m.p. 145—146°, b.p. 185°/2 mm. (*P* 0·40±0·08), -n-*butyl*-, b.p. 178—180°/1 mm. (*P* 0·37±0·12), -n-*amyl*- (**II**) (*P* 1·00), -n-*hexyl*-, b.p. 190—192°/1 mm. (*P* 1·82±0·18), -n-*heptyl*-, b.p. 225—228°/0·05 mm. (*P* 1·05±0·15), and -n-*octyl*-, b.p. 215—220°/0·01 mm. (*P* 0·66±0·12), -3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyran*. 6″-Hydroxy-2 : 2 : 5′ : 4″-tetramethyl-3′ : 4′ : 5′ : 6′-tetrahydro-3 : 4 : 5 : 6-dibenzpyran, has *P* <0·2. 5-n-*Octylresorcinol* has b.p. 164—168°/4 mm.

X. 6″-Hydroxy-5′-methyl-4″-*n*-amyl-3′ : 4′ : 5′ : 6′-tetrahydro-3 : 4 : 5 : 6-dibenzpyrone [modified prep. from (**I**) and olivetol (**III**) by $POCl_3$–C_6H_6] with MgEtBr or $MgPr^nBr$ gives 6″-*hydroxy*-5′-*methyl*-3 : 3-*diethyl*-, b.p. 185—195°/0·02 mm. (*P* 0·12±0·024), and -*di*-n-*propyl*-, b.p. 200—204°/2 mm. (*P* 0·04±0·01), -4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydrodibenzpyran*. Et 4- or 6-methyl*cyclo*hexanone-2-carboxylate, (**III**), and $POCl_3$ in C_6H_6 give 6″-*hydroxy*-4′-, m.p. 169—169·5°, and -6′-*methyl*-4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyrone*, m.p. 194—194·5°, and thence 6″-*hydroxy*-2 : 2 : 4′-m.p. 72—73° (*P* 0·137±0·01), and -2 : 2 : 6′-*trimethyl*-4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyran*, b.p. 181—185°/0·5—1·0 mm. (*P* 0·25±0·05). Et *cyclo*hexanone-2-carboxylate and (**III**) similarly give 6″-*hydroxy*-4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyrone*, m.p. 183—183·5°, and thence 6″-*hydroxy*-2 : 2-*dimethyl*-4″-n-*amyl*-3′ : 4′ : 5′ : 6′-*tetrahydro*-3 : 4 : 5 : 6-*dibenzpyran*, b.p. 175—180°/0·02 mm. (*P* 0·126±0·05). Condensation of pulegone and orcinol (**IV**) or olivetol gives compounds, as (**II**) but impure (absorption spectra), [α] depending on the amount of $POCl_3$ used; that corresponding with (**II**) has *P* 1·04±0·37 (cf. Ghosh *et al.*, A., 1941, II, 145).

XI. $CH_2Ac{\cdot}CO_2Et$ (**V**) and (**IV**) in 85% H_3PO_4 give 5-hydroxy-4 : 7-dimethylcoumarin, m.p. 258—259° (lit. 250°). (**V**), (**III**), and $POCl_3$ in boiling C_6H_6 give 5-*hydroxy*-4-*methyl*-7-n-*amylcoumarin*, m.p. 178—179°, converted by MgMeI in Bu_2O at 90° into 5-*hydroxy*-2 : 2 : 4-*trimethyl*-7-n-*amyl*-1 : 2-*benzpyran*, b.p. 140—142°/0·02 mm. (*P* 0·033±0·01). $CHBu^nAc{\cdot}CO_2Et$ with (**IV**) or (**III**) and $POCl_3$ in C_6H_6 at room temp. give 5-*hydroxy*-4 : 7-*dimethyl*-3-n-*butylcoumarin* (62%), m.p. 191—195° (and a trace of ? 7-hydroxy-4 : 5-dimethyl-3-*n*-butylcoumarin, m.p. 158—159°), and 5-*hydroxy*-4-*methyl*-3-n-*butyl*-7-n-*amylcoumarin* (66%), m.p. 140·5—141°, respectively, and from the latter 5-*hydroxy*-2 : 2 : 4-*trimethyl*-3-n-*butyl*-7-n-*amyl*-1 : 2-*benzpyran*, b.p. 176—177°/0·05 mm. (*P* 0·04±0·01). R. S. C.

Photochemistry of fluorescein dyes.—See A., 1941, I, 423.

2 : 6-Diohlorodiphenylene dioxide. S. Uyeo (*Bull. Chem. Soc. Japan*, 1941, **16**, 177—179).—2 : 6-Dinitrodiphenylene dioxide, m.p. 262°, and H_2–Pd–C in AcOH give quantitatively the $(NH_2)_2$-compound, m.p. 249°, which by a Sandmeyer reaction yields 2 : 6-*dichlorodiphenylene dioxide* (**I**), m.p. 207°. The dipole moment [Higasi], 0·62, of (**I**) indicates a folded structure and is < that (0·64) of diphenylene dioxide. R. S. C.

Aluminium chloride, a new reagent for the condensation of β-ketonic esters with phenols. V. Condensation of substituted resacetophenones with ethyl acetoacetate. C. V. Deliwala and N. M. Shah (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 352—358; cf. A., 1938, II, 152).—5-Ethylresacetophenone condenses with $CH_2Ac{\cdot}CO_2Et$ in dry $PhNO_2$ containing $AlCl_3$ at ~115° to 5-hydroxy-6-acetyl-4-methyl-8-ethylcoumarin, m.p. 168—169° (cf. Desai *et al.*, A., 1939, II, 173), reduced (Clemmensen) to 5-hydroxy-4-methyl-6 : 8-diethylcoumarin, m.p. 171°, and acetylated (Kostanecki) to 3′-acetyl-4 : 2′-dimethyl-6′-ethyl-7′ : 8′ : 6 : 5-chromono-α-pyrone, m.p. 173°. Condensation cannot be effected by conc. H_2SO_4. 5-Bromoresacetophenone and $CH_2Ac{\cdot}CO_2Et$ in dry $PhNO_2$ containing $AlCl_3$ at 115—120° and subsequently at 130° give 8-*bromo*-5-*hydroxy*-6-*acetyl*-4-*methylcoumarin*, m.p. 208—210° (*acetate*, m.p. 150°; *oxime*, m.p. >250°), which gives a cherry-red colour with $FeCl_3$ and a non-fluorescent, yellow solution in alkali; it is transformed by Ac_2O and NaOAc at 170—180° into 6′-*bromo*-4 : 2′-*dimethylchromono*-7′ : 8′-6 : 5-α-*pyrone*, m.p. 240—241°. Condensation does not succeed in the presence of $POCl_3$ or H_2SO_4. 5-Nitro-, 5-benzyl-, and ω-methoxy-resacetophenone, Me β-resacetophenonecarboxylate, 4 : 6- and 2 : 4-diacetylresorcinol do not condense or yield tarry material. 4 : 1-$C_{10}H_6Ac{\cdot}OH$ and $CH_2Ac{\cdot}CO_2Et$ afford 4-methyl-1 : 2-α-naphthapyrone, m.p. 172°, obtained also from 4 : 1-$COEt{\cdot}C_{10}H_6{\cdot}OH$. H. W.

Sulphur. XVII. Synthesis of sulphathiophen, 2-sulphanilamidothiophen. R. W. Bost and C. F. Starnes (*J. Amer. Chem. Soc.*, 1941, **63**, 1885—1886; cf. A., 1940, II, 296).—2-Aminothiophen stannichloride (modified prep.) and *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ give 2-N^4-*acetylsulphanilamido*-, m.p. 196°, and thence (10·4% H_2SO_4) 2-*sulphanilamido*-*thiophen*, m.p. 156·5—157·5°. R. S. C.

Phenylhydantoins. H. R. Henze and L. M. Long (*J. Amer. Chem. Soc.*, 1941, **63**, 1936—1938).—$COPh{\cdot}[CH_2]_3{\cdot}Ph$, $(NH_4)_2CO_3$, and KCN in 50% EtOH at 60° give 5-*phenyl*-5-β-*phenylethylhydantoin* (67%), m.p. 201° (Na salt, strong anticonvulsant), which with Na and then Me_2SO_4 in abs. EtOH gives 5-*phenyl*-5-β-*phenylethyl*-3-*methylhydantoin* (not anticonvulsant), m.p. 144°. $COPh{\cdot}C_{11}H_{23}$-*n*, $(NH_4)_2CO_3$, and KCN in NH_2Ac at 110° give 5-*phenyl*-5-n-*undecylhydantoin*, m.p. 125°. $COR{\cdot}CH{:}CHPh$, $(NH_4)_2CO_3$, and KCN in H_2O at 59° or 60° give 5-styryl-5-methyl-, m.p. 222—223° [lit. 217° (decomp.)], -5-*ethyl*-, m.p. 214°, -5-n-*propyl*-, m.p. 171—174°, and -5-n-*butyl*-*hydantoin*, m.p. 125—130°. 5-Phenylhydantoin and Br–AcOH give the 5-Br-derivative, m.p. 210—215°, which with COPhMe at ~70° gives 5-*phenyl*-5-*phenacylhydantoin*, m.p. 221°. With KCN and $(NH_4)_2CO_3$ in $OH{\cdot}[CH_2]_3{\cdot}OH$ at 110° this gives 5 : 5′-*methylenebis*-5-*phenylhydantoin*, m.p. 358° (decomp.). M.p. are corr. R. S. C.

Reactions of 2-aminopyridine with diketones. I. Reaction of 2-aminopyridine with benzil. P. G. Sokov (*J. Gen. Chem. Russ.*, 1940, **10**, 1457—1461).—2-Aminopyridine (**I**) and benzil (60—90 min. at 200—225°) yield α-2-*pyridylaminodiphenylacetic acid*, melting with decomp. at 156°, giving 2-*pyridylaminodiphenylmethane* [2-*benzhydrylaminopyridine*], m.p. 104—105° (*hydrochloride*, m.p. 190—191°; *hydrobromide*, m.p. 195—196°; *picrate*, m.p. 183—184°), also prepared from (**I**) and $CHPh_2Br$, or from (**I**) and $OH{\cdot}CPh_2{\cdot}CO_2H$. R. T.

Preparation of sulphapyridine. B. Bobrański and I. M. Eker (*J. Appl. Chem. Russ.*, 1940, **13**, 1637—1641).—A 1 : 2 mixture of *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ and 2-aminopyridine heated for 1 hr. at 100° gives acetylsulphapyridine (64% yield). This, heated for 1 hr. at 58—62° with 15% HCl, gives sulphapyridine in 75% yield. R. T.

Synthesis of 3-ethylpyridine. T. Ikeda and C. Ashizawa (*J. Pharm. Soc. Japan*, 1941, **61**, 42—45).—Nicotinoyl chloride hydrochloride and CH_2N_2 in dry Et_2O give a dark red resin, converted by warm AcOH into 3-acetoxyacetylpyridine, m.p. 83—84°, in very poor yield. 3-Acetylpyridine (hydrochloride, m.p. 174—177°; *semicarbazone*, m.p. 207—208°),

from Et nicotinate and EtOAc followed by boiling 10% HCl, is reduced by N_2H_4,H_2O at 120—130° followed by KOH at 150° to 3-ethylpyridine (picrate, m.p. 125—128°) and the *azine*, $C_{14}H_{14}N_4$, m.p. 108—109° (*dipicrate*, decomp. 241°). N_2H_4 *picrate*, decomp. 190°, is incidentally described. H. W.

Preparation of indole. F. T. Tyson (*J. Amer. Chem. Soc.*, 1941, **63**, 2024—2025).—Indole is best (46%) obtained from *o*-$C_6H_4Me{\cdot}NH{\cdot}CHO$ by $KOBu^{\gamma}$ (1·5 mol.) at 350—360°. Other proportions or use of KNH_2–NH_3, KOMe, or KOEt is less satisfactory and Na salts are useless. R. S. C.

7-Bromo-5-iodoisatin and 3-bromo-5-iodo-2-aminobenzoic acid. W. C. Sumpter (*J. Amer. Chem. Soc.*, 1941, **63**, 2027—2028).—5-Iodoisatin and Br in boiling EtOH give *7-bromo-5-iodoisatin*, m.p. 247—248°, which with 3% H_2O_2 in alkali gives *3-bromo-5-iodo-2-aminobenzoic acid*, m.p. 226—227°, also obtained from 2 : 5 : 1-$NH_2{\cdot}C_6H_3I{\cdot}CO_2H$ by Br–EtOH. 5-Bromoisatin is unaffected by ICl. R. S. C.

Preparation of 1-acyl-1 : 2-dihydroquinoline-2-nitriles and their hydrolysis to aldehydes. J. M. Grosheintz and H. O. L. Fischer (*J. Amer. Chem. Soc.*, 1941, **63**, 2021—2022).—RCOCl, HCN, and quinoline (1 : 1 : 2 mols.) in C_6H_6 at −5° and later room temp. (16 hr.) give usually 64—96% of *2-cyano-1-acetyl-*, m.p. 96—97°, *-propionyl-* (10%), m.p. 49—50°, -benzoyl-, m.p. 154—155°, -cinnamoyl-, m.p. 154—155°, -n-, m.p. 97·5—98°, and -iso-*butyryl-*, m.p. 129—129·5°, -iso*valeryl-*, m.p. 90—90·5°, -o-, m.p. 164—164·5°, and -p-*anisoyl-*, m.p. 120·5—121·5°, -o-, m.p. 165—166°, -m-, m.p. 116—119°, and -p-*chlorobenzoyl-*, m.p. 140—143°, -1 : 2-*dihydroquinoline*, which yield 90% of RCHO and quinoline-2-carboxylic acid when the acid (5—10N-H_2SO_4) solution is distilled in steam. For direct prep. of aldehydes from acids, isolation of RCOCl and the nitrile is unnecessary. $CHR{:}N{\cdot}NH{\cdot}C_6H_3{\cdot}NO_2$-*p* are reported in which R = Me, m.p. 127·5—128°, Et, m.p. 128—129°, Pr$^{\alpha}$, m.p. 90—91°, Pr$^{\beta}$, m.p. 131·5—132°, *o*-, m.p. 208°, and *p*-$OMe{\cdot}C_6H_4$, m.p. 162°, *o*-, m.p. 247—248°, *m*-, m.p. 220°, and *p*-C_6H_4Cl, m.p. 219°, $CHPh{:}CH$, m.p. 169·5—170·5°, and Ph, m.p. 193—194°, and $CHR{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$-2 : 4 in which R = Bu$^{\alpha}$, m.p. 96—98°, and Bu$^{\beta}$, m.p. 122—123°. R. S. C.

Condensation of ethylaniline with acetylene in presence of $HgCl_2$. I. F. Kriuk (*J. Gen. Chem. Russ.*, 1940, **10**, 1507—1509).—A solution of NHPhEt and $HgCl_2$ in EtOH, saturated with C_2H_2, yields indole (**I**) and quinaldine (**II**) by the reactions: $NHPhEt + C_2H_2 \rightarrow NPhEt{\cdot}CH{:}CH_2$ (**III**); 2(**III**) $\rightarrow$ $NPhEt{\cdot}CHMe{\cdot}CH{:}CH{\cdot}NPhEt \rightarrow$ (**I**) + (**II**) + C_2H_6 + $2H_2$. R. T.

Acridine derivatives. VI. S. J. Das-Gupta (*J. Indian Chem. Soc.*, 1941, **18**, 25—28; cf. A., 1939, II, 364).—The hydrochlorides, m.p. 187° and 257°, respectively, of 4 : 2 : 1- or 5 : 2 : 1-$NH_2{\cdot}C_6H_3Cl{\cdot}CO_2H$, and *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$–aq. Na_2CO_3 afford *2-chloro-4*, m.p. 142°, and *-5-(p-acetamidobenzene)sulphonamidobenzoic acid*, m.p. 263°, converted by *p*-$NH_2{\cdot}C_6H_4{\cdot}OMe$–$K_2CO_3$–$C_5H_{11}{\cdot}OH$–Cu powder into 4-, m.p. 158—160°, and 5-(p-*acetamidobenzene)sulphonamido-4'-methoxydiphenylamine-2-carboxylic acid*, m.p. 218—220°, and thence by $POCl_3$ at 100° (bath) into *5-chloro-2-*, m.p. 245—247° (decomp.), and *-3-(4'-acetamidobenzene)sulphonamido-7-methoxyacridine* (**I**), m.p. 243—244° (decomp.) (hydrolysed by aq. HCl–EtOH to the corresponding *4'-NH_2*-compound, m.p. ~180°). Equimols. of 2 : 5-dichloro-7-methoxyacridine and *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$, *p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NEt_2$, or *p*-$NH_2{\cdot}C_6H_4{\cdot}NHAc$ in PhOH at 110—120°, 120°, or 150—160°, respectively, give N^4-*(2-chloro-7-methoxy)acridylaminobenzenesulphon-amide*, m.p. 286°, *-diethylamide*, m.p. 175° (hydrochloride, m.p. 260—261°), or *-acetamide*, m.p. 248—250°. Similarly prepared are N^4-*(7-methoxy)acridylaminobenzenesulphon-diethylamide*, m.p. 263—264°, and *-acetamide*, m.p. 143—145°. A. T. P.

Acridine synthesis and reactions. II. Synthesis of proflavine from *m*-phenylenediamine and its derivatives (continued). A. Albert (*J.C.S.*, 1941, 484—487; cf. A., 1941, II, 148).—By interrupting the reaction between *m*-$C_6H_4(NH_2)_2$ (*picrate*, m.p. 184°) and glycerol with $H_2C_2O_4$ or HCO_2H at 140° after 10 min. and neutralising (aq. NH_3) the cooled, diluted melt, 3 : 3'-*diamino*-N-*formyldiphenylamine* (**I**), m.p. 138·5°, N-2' : 4'-*diamino-α-hydroxybenzyl*-m-*phenylenediamine* (**II**), m.p. ~120° (decomp.), and *bis*-2 : 4 : 2' : 4'-*tetra-aminobenzhydryl ether* (**III**), m.p. ~295° (decomp.), are obtained. $NHPh{\cdot}C_6H_4{\cdot}NO_2$-*m*, $ZnCl_2$, and HCO_2H give *3-nitro-N-formyldiphenylamine*, m.p. 77°, reduced to the 3-NH_2-compound, m.p. 131—132° (decomp.); 3 : 3'-*dinitro-N-formyldiphenylamine*, m.p. 145—146°, similarly prepared, is reduced to (**I**). By heating *m*-$C_6H_4(NH_2)_2$ with HCO_2H and H_3BO_3 in distilling PhMe, (**II**) is obtained and when this is warmed with HCl in glycerol, a 75% yield of proflavine (**IV**) is formed. $CO[C_6H_3(NH_2)_2$-2 : 4$]_2$ is reduced to 2 : 4 : 2' : 4'-*tetra-aminobenzhydrol*, decomp. 200°, remelts 290°, which is formed when (**III**) is hydrolysed in 50% aq. $COMe_2$ with HCl. It is concluded that the dihydrochloride of (anhydro)-2 : 4 : 2' : 4'-tetra-aminobenzhydrol is the immediate precursor of (**IV**). F. R. S.

5-4'-Diphenylyl-5-R-hydantoins and 4 : 4'-diphenylylenebis-5:5-R-hydantoins. H. R. Henze and L. M. Long (*J. Amer. Chem. Soc.*, 1941, **63**, 1941—1943).—*p*-$C_6H_4Ph{\cdot}COR$ and KCN in NH_2Ac at 110° give 71—90% of 5-4'-diphenylyl-5-*methyl-*, m.p. 295°, *-5-ethyl-*, m.p. 256°, -5-n-, m.p. 201·5—202·5°, and -5-iso-*propyl-*, m.p. 270—271°, -5-n-, m.p. 199·5°, and -5-iso-*butyl-*, m.p. 224—225°, -5-n-, m.p. 195—196·5°, and -5-iso-*amyl-*, m.p. 232—233°, *-5-α-methyl*-n-*butyl-*, m.p. 262°, *-5-α-ethyl*-n-*propyl-*, m.p. 249—250°, -5-phenyl-, m.p. 242°, and -5-n-*hexyl-*, m.p. 185—186·5°, *-hydantoin*. (*p*-$C_6H_4{\cdot}COR)_2$ gives similarly 53—80% of 4 : 4'-*diphenylene-bis-5-5-methyl-*, m.p. 360°, *-ethyl-*, m.p. 335°, -n-, m.p. 214°, and -iso-*propyl-*, m.p. 360°, -n-, m.p. 310°, and -iso-*butyl-*, m.p. 295°, -n-, m.p. 312°, and -iso-*amyl-*, m.p. 335°, -n-*hexyl-*, m.p. 284°, and *-phenyl-*, m.p. 282°, *-hydantoin*. M.p. are corr. R. S. C.

Hydantoins. I. A. Novelli (*Anal. Asoc. Quim. Argentina*, 1941, **29**, 83—87).—The following hydantoins, prepared from ketones, KCN, and $(NH_4)_2CO_3$ (cf. Bucherer and Steiner, A., 1934, 1231), are described: 5 : 5-o-*diphenylene-*, decomp. 308—310°, 5 : 5-o-*phenylenetrimethylene-*, m.p. 237·5—239·5° (from α-tetralone), 5 : 5-2'-*methyl*-5'-iso*propyl*cyclo*penta-methylene-*, m.p. 217—219°, 5-3'-*phenanthryl-5-methyl-*, m.p. 232—235°, 5-2'-*phenanthryl-5-ethyl-*, m.p. 315—317°. F. R. G.

Synthesis of *N*-disubstituted 5-phenylethyl-5-aminomethylhydantoins. H. R. Henze and C. B. Holder (*J. Amer. Chem. Soc.*, 1941, **63**, 1943—1945).—*α-Chloro-δ-phenylbutan-β-ol*, m.p. 46—47°, b.p. 112—114°/4 mm., and CrO_3 give $Cl{\cdot}[CH_2]_2{\cdot}COPh$, m.p. 40—41° (lit. 84—85°), b.p. 110·5—111·5°/5 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 147·2—147·7°), which with $NHMe_2$,HCl and Na_2CO_3 in aq. $COMe_2$ at <0° or NHR_2 (2 equivs.) in Et_2O or C_6H_6 at 0° gives *α-dimethyl-*, b.p. 106—107°/3·5 mm. (*picrate*, m.p. 118—119°), *-ethyl-*, b.p. 119°/4 mm. (*picrate*, m.p. 104·5—105·5°, -n-*propyl-*, b.p. 136—138°/4 mm. (*picrate*, m.p. 116·5—117·5°), -n-*butyl-*, b.p. 159—160°/5·5 mm. (*picrate*, m.p. 99—100°), and -iso-*amyl-*, b.p. 161—163°/4 mm. (*picrate*, an oil), *-amino-δ-phenylbutan-β-one* and *α-morpholino-δ-phenylbutan-β-one*, m.p. 23—24°, b.p. 180—181°/7 mm. (*picrate*, m.p. 136·3—137·3°). With KCN and $(NH_4)_2CO_3$ in 50—65% EtOH at 58—60° these give *5-β-phenylethyl-5-dimethyl-*, m.p. 232·3—233·3°, *-ethyl-*, m.p. 203·3—205·3°, -n-*propyl-*, m.p. 196·5—197·5°, -n-*butyl-*, m.p. 161—163°, and -iso*amyl-*, m.p. 124·7—127·2°, *-aminohydantoin*. *5-β-Phenylethyl-5-NN-phenylethylamino-*, m.p. 176—177·5°, and *-5-morpholino-hydantoin*, m.p. 222—223°, are also prepared. M.p. are corr. R. S. C.

Action of diazomethane on lactones and lignins. E. Y. Spencer and G. F. Wright (*J. Amer. Chem. Soc.*, 1941, **63**, 2017—2020).—The so-called phenolic OH content, determined by CH_2N_2, is not characteristic of native lignin as it depends on the method of extraction. *E.g.*, bound phenolic OH is present in Et_2O-sol. birch lignin extracted by Ac_2O; CH_2N_2 raises the OMe from 19·7 to 21·9%, but after hydrolysis by 10% alkali from 23·3 to 34% (some xylosazone is obtained after hydrolysis). Further, CH_2N_2 reacts with lactones; *e.g.*, valerolactone gives $OH{\cdot}[CH_2]_2{\cdot}CO_2Me$, identified as acetate, and coumarin gives *Me 3-o-anisylpyrazoline-4-carboxylate*, m.p. 94·5°. Lignin probably contains coumarin linkings since the N content is raised from 0 to nearly 1% by treatment with CH_2N_2. R. S. C.

Interaction of organic sulphur compounds with hydrogen peroxide. XXI. Mechanism of desulphurisation of thiopyrine to antipyrine by hydrogen peroxide. II. R. Kitamura and T. Ōno (*J. Pharm. Soc. Japan*, 1941, **61**, 17—19; cf. A., 1939, II, 456).—5-Thiopyrine and H_2O_2 (2 mols.) in MeOH give a crude oily dioxide (**I**), converted by distillation into SO_2 and 1-*phenyl-3-methylpyrazole*, m.p. 34·5—35·5°, b.p.

143—145°/18 mm., also obtained from 5-chloro-1-phenyl-3-methylpyrazole by P–HI and oxidised by $KMnO_4$–KOH to 1-phenylpyrazole-3-carboxylic acid. 3-Thiopyrine similarly gives 1-*phenyl-5-methylpyrazole*, b.p. 140—143°/20 mm., oxidised to 1-phenylpyrazole-5-carboxylic acid. The reaction mechanism is discussed. R. S. C.

Reaction between organic sulphur compounds and hydrogen peroxide. XXII. Mechanism of the desulphurisation of thiopyrine (→ antipyrine) by hydrogen peroxide. III. Synthesis of tetrabromothiopyrine dioxide and the consideration of the mechanism of desulphurisation. R. Kitamura (*J. Pharm. Soc. Japan*, 1941, **61**, 39—42).—A study of the behaviour of thiopyrine (**I**) towards H_2O_2 followed by Br and towards Br alone or in presence of HBr in aq. and non-aq. medium leads to the following conclusions. (**I**) and its homologues are converted by H_2O_2 into a dioxide (**II**) and then a trioxide (**III**) from which desulphurisation occurs. Desulphurisation at the greatest rate occurs mainly from (**II**); little part is played by (**III**) and the change is rapidly completed. With compounds which react less readily a relatively greater amount of (**III**) is formed and this consequently has a more pronounced function in the desulphurisation. The first type of action is best shown by 1 : 2-diphenyl-3-methyl-5-thiopyrazole with the slowest oscillation and the second type by 1 : 2 : 3-trimethyl-5-pyrazole with its most rapid oscillation. With this compound the trioxide is the main initial material in desulphurisation and the process is therefore incomplete at room temp. (**I**, dithio-, di- and 3-thiopyrine resemble one another and are placed between the two extreme classes; nevertheless with these substances desulphurisation takes place mainly from the dioxide and is generally complete. (**I**) and its hypothetical monoxide are rapidly converted by H_2O_2 into the dioxide. H. W.

Oscillation state and reactivity. Constitution of antipyrine and related compounds. IX. Comparison of 1 : 2-diphenyl-3-methyl-5-thiopyrazole and analogous compounds. X. Products of the reaction of thiopyrine with bromine water. R. Kitamura. **XI. Derivatives of antipyrine.** R. Kitamura and G. Sunagawa (*J. Pharm. Soc. Japan*, 1941, **61**, 8—12, 12—14, 14—17; cf. A., 1941, II, 304).—IX. Relative rates of desulphurisation by H_2O_2–KOH are 1 : 2-*diphenyl-5-methyl*- (**I**) > 1-phenyl-2 : 3-dimethyl- > 1 : 2 : 3-trimethyl-5-thiopyrazole (**II**). 5-Keto-1 : 2-diphenyl-3-methylpyrazole (**III**) and $POCl_3$ give 5-*chloro*-1 : 2-*diphenyl-3-methylpyrazole chloride* (**IV**), m.p. 234—237°, converted by KSH into (**I**), m.p. 185—186°, b.p. 243—244°/0·01 mm., yellow and colourless *forms*. Aq. Cl_2 converts (**I**) into the *trioxide*, decomp. 263—265°, which is better obtained from (**IV**) by Na_2SO_3, is desulphurised faster than is (**I**), and is converted by 2N-KOH into (**III**). (**II**) also exists in yellow and colourless forms and with neutral H_2O_2 gives the trioxide (**V**), decomp. 274—276°, or later 5-keto-1 : 2 : 3-trimethylpyrazole (**VI**), also obtained from (**V**) by boiling KOH. The first step in desulphurisation of (**II**) by alkaline H_2O_2 is formation of the dioxide, which is mainly converted into (**V**) and thence (**VI**) and to a small extent yields (**VI**) directly. The results are explained by means of the oscillation theory.

X. 5-Keto-1-phenyl-2 : 3-dimethylpyrazole absorbs 7—8 Br in H_2O to give the *compound*, $\begin{matrix}NMe\cdot NPhBr\\ |\\ CMe{=}CH\end{matrix}\!\!>\!C\cdot SBr(OBr)_2$, decomp. 112—113° (cf. Komata, *J. Chem. Soc. Japan*, 1938, **59**, 482). In warm H_2O or cold N-Na_2CO_3 or -KOH this gives Br and the trioxide, decomp. ~300°, and yields the Br quantitatively to 0·1N-KOH at 100° in 5 min. or at room temp. in 2 days.

XI. Antipyrine and NaOCl (2 mols.) in 2N-NaOH give 4-chloroantipyrine (**VII**), m.p. 126—127°, and an oil, converted by warm H_2O into (**VII**) (cf. Leulier, A., 1924, i, 875; Komata, *J. Chem. Soc. Japan*, 1937, **58**, 1305). With $POCl_3$, (**VII**) gives 4 : 5-dichloro-1-phenyl-3-methylpyrazole (**VIII**), m.p. 54—55°, and the *methochloride* (**IX**), decomp. 173—178° [yields (**VIII**)], thereof. With conc. aq. KSH, (**IX**) gives 1-phenyl-2 : 3-dimethyl-5-thiopyrazole, converted by H_2O_2–NaOH into (**VIII**). Na_2SO_3 and (**IX**) give 4-chloro-1-phenyl-2 : 3-dimethyl-5-thiopyrazole trioxide, rapidly converted into (**VIII**) by H_2O_2–NaOH or boiling KOH. R. S. C.

Pyrimidines. CLXXII. Hydrogenolysis of 4-iminobarbituric acid. J. C. Ambelang and T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 1934—1935; cf. A., 1941, II, 270).—Hydrogenation (PtO_2; ~80°/2·5 atm.; H_2O) of 4-iminobarbituric acid causes fission of the $C_{(4)}$–N linking (giving uracil), which supports the structure assigned to toxoflavine I. 5 : 5-*Dichloro*-2 : 4-*diketo*-2-*ethoxyhexahydropyrimidine*, m.p. 230° (decomp.), is prepared by chlorination in abs. EtOH. R. S. C.

Polarisation in heterocyclic rings with aromatic character. XIV. Syntheses of pyrimidine and dipyrimidyl homologues. M. Yanai and T. Naito (*J. Pharm. Soc. Japan*, 1941, **61**, 46—53).—Et hexoylacctoacetate and NH_3 in cold Et_2O yield Et hexoylacetate (**I**), b.p. 127—130°/20 mm. (*Cu* compound, m.p. 107°), NH_2Ac, and hexoamide, m.p. 100°. (**I**), NaOEt, and $CS(NH_2)_2$ in boiling EtOH yield 6-*amyl*-2-*thiouracil*, m.p. 151—153°, transformed by 0·1N-KOH and 3% H_2O_2 at 20° into 6-*amyluracil*, m.p. 171—173°; this with $POCl_3$ at 120° affords 2 : 4-*dichloro*-6-*amylpyrimidine*, b.p. 130—135°/3 mm., which with H_2–Pd–$CaCO_3$ in MeOH gives 6-*amylpyrimidine*, b.p. 130—135° (bath)/0·05 mm. (*aurichloride*, m.p. 110—112°; *platinichloride*, decomp. 208°). *Valeroamidine hydrochloride* (corresponding *picrate*, m.p. 190°) and $CH_2Ac\cdot CO_2Et$ are converted by 10% KOH–EtOH at room temp. into 4-*hydroxy*-6-*methyl*-2-n-*butylpyrimidine* (**II**), m.p. 120°, transformed by boiling $POCl_3$ into 4-*chloro*- (**III**), b.p. 110—115° (bath)/3 mm., whence are derived 4-*amino*-6-*methyl*-2-n-*butylpyrimidine*, m.p. 97°, and 6-*methyl*-2-n-*butylpyrimidine*, b.p. 130—135° (bath)/5 mm. (*platinichloride*, m.p. 186°). *Et valeroylacetoacetate*, b.p. 115—118°/5 mm. (*Cu* salt, m.p. 55·5°), from $Bu^{\alpha}COCl$, $CH_2Ac\cdot CO_2Et$, and Mg turnings in C_6H_6 at 80—85°, is slowly transformed by boiling H_2O into valeroylacetone (*Cu* salt, m.p. 137°), which condenses with $CO(NH_2)_2$ and conc. HCl in abs. EtOH to *diuramidovaleroylacetone*, m.p. 144°, as main product. (**III**) is converted by Cu-bronze in boiling cumene into 6 : 6′-*dimethyl*-2 : 2′-*di*-n-*butyl*-4 : 4′-*dipyrimidyl*, b.p. 180—185° (bath)/0·01 mm. (*hydrochloride*, m.p. 247°). 4-Chloro-2-benzyl-6-methylpyrimidine and HI (*d* 1·7) at room temp. and then at 50° yield the 4-*I*-compound, m.p. 127°, transformed by Cu-bronze in boiling cumene into 2 : 2′-*dibenzyl*-6 : 6′-*dimethyl*-4 : 4′-*dipyrimidyl*, m.p. 199°. Cu-bronze converts 2-chloro-4-benzyl-6-methylpyrimidine in cumene, tetrahydronaphthalene, or without solvent into an unidentified *compound*, $C_{21}H_{20}N_4Cl_2$, m.p. 226°, and HI transforms it into 4-benzyl-6-methylpyrimidine. (**III**) and HI yield (**II**). 2 : 4-Dichloro- and HI (*d* 1·7) at room temp. afford *chloroiodo*-, m.p. 90°, and 2 : 4-*di-iodo*-, m.p. 161°, -6-*methylpyrimidine*. The last-named reacts with difficulty with Cu-bronze, giving a small proportion of *substance*, m.p. 185—189°, and appears to be unchanged by Na. H. W.

Pyrazine series. III. Amination of 2 : 5-dimethylpyrazine. Synthesis of 3-sulphanilamido-2 : 5-dimethylpyrazine. R. R. Joiner and P. E. Spoerri (*J. Amer. Chem. Soc.*, 1941, **63**, 1929—1930; cf. A., 1940, II, 193).—2 : 5-Dimethylpyrazine and $NaNH_2$ in $NPhMe_2$ at 165° give 35% of the 3-NH_2-derivative, m.p. 111—112°, b.p. 119—122°/10 mm. (cf. Tschitschibabin *et al.*, A., 1931, 100), which with *p*-$NHAc\cdot C_6H_4\cdot SO_2Cl$ in C_5H_5N at <50° gives 3-N⁴-*acetylsulphanilamido*-, m.p. 238—239°, and thence (6N-HCl; 100°) 3-*sulphanilamido*-2 : 5-*dimethylpyrazine*, m.p. 227—228° (corr.). R. S. C.

Synthesis of substances of probable antimalarial action. I. Structure and pharmacological properties. II. Benzimidazole compounds with a γ-diethylaminopropyl group. V. A. Izmailski and A. M. Simonov (*J. Gen. Chem. Russ.*, 1940, **10**, 1580—1587, 1588—1599).—I. 3-*Amino*-4-*benzamidoanisole* (**I**), m.p. 200—200·5° (prepared by reduction of the corresponding 3-NO_2-compound), condenses with PhCHO to 3-*benzylideneamino*-4-*benzamidoanisole*, m.p. 96—97°. With HNO_2 (**I**) yields 1-*benzoyl*-5-*methoxy*-1 : 2 : 3-*benztriazole*, m.p. 116°. (**I**) with $NEt_2\cdot[CH_2]_3\cdot Cl$ (**II**) (2 hr. at 110—115°, then 3 hr. at 130—135°, then 10 hr. at 150—155°) gives 4-*benzamido*-3-(N-γ-*diethylaminopropyl*)*aminoanisole*, m.p. 143·5—144°, which had no antimalarial properties. 3-*Amino*-4-*benzenesulphonamidoanisole*, m.p. 116·5—117·5°, is prepared by reduction of the corresponding 3-NO_2-compound. Attempts to condense this compound with (**II**) were unsuccessful.

II. 3-Nitro-4-(*p*-toluenesulphonamido)anisole and (**II**) in EtOH, in presence of K_2CO_3 (12 hr. at the b.p.), yield 3-*nitro*-4-(p-*toluenesulphonyl*-γ-*diethylaminopropyl*)*aminoanisole*, m.p. 77·5—78°. This is dissolved in 90% H_2SO_4, and the solution is made neutral with aq. NH_3 after 12 hr., giving 3-*nitro*-4-(γ-*diethylaminopropyl*)*aminoanisole*, b.p. 191·5—193·5°/2·5 mm. (*picrate*, melting at 114—115°, to yield a chromo-isomeride, m.p. 126—127°), reduced by $SnCl_2$ in HCl to 3-*amino*-4-

(*γ-diethylaminopropyl*)*aminoanisole*, b.p. 196—198°/4 mm. This with Ac_2O in HCl (90 min. at the b.p.) yields 5-*methoxy*-2-*methyl*-1-(*γ-diethylaminopropyl*)*benziminazole* (**III**), b.p. 184—185°/2 mm. (*dipicrate*, m.p. 236°). 3-Amino-4-acetamidoanisole (**IV**) and PhCHO in EtOH yield 3-*benzylideneamino*-4-*acetamidoanisole*, m.p. 128—128·5°. (**IV**) and 1 : 2 : 4-$C_6H_3Cl(NO_2)_2$ yield 2 : 4-*dinitro*-2′-*acetamido*-5-*methoxydiphenylamine*, m.p. 263·5°. (**IV**) condenses with (**II**) in EtOH (3 hr. at 110—115°, then 13 hr. at 135—140°) to 6-*methoxy*-2-*methyl*-1-(*γ-diethylaminopropyl*)*benziminazole* (**V**), b.p. 190·5—191·5°/2 mm. [*dipicrate*, m.p. 218·5—219° (decomp.)]. This with PhCHO (3—4 hr. at 200°) yields 6-*methoxy*-2-*styryl*-1-(*γ-diethylaminopropyl*)*benziminazole* (*dihydrochloride*, m.p. 234—236°). A solution of (**IV**) in AcOH–HCl, heated at the b.p. for 1 hr., yields 5(6)-*methoxy*-2-*methylbenziminazole*, m.p. 141·5—142·5° (*picrate*, m.p. 191·5—192·5°), which with (**II**) (3—4 hr. at 110—115°) gives a mixture of (**III**) and (**V**). None of the above-described products have any antimalarial action. R. T.

Polarisation in heterocyclic rings having aromatic character. XIII. Polarisation in pyrimidine rings. E. Ochiai and M. Yanai (*J. Pharm. Soc. Japan*, 1940, **60**, 192—199; cf. A., 1941, II, 149).—2-Aminopyrimidine and picryl chloride (**I**) in C_6H_6 give 4 : 6-*dinitropyrimidino*-(1′ : 2′-2 : 1)-*benziminazole*, m.p. 196° (decomp.), whereas 4-aminopyrimidine affords picramide and 4-hydroxypyrimidine. 2-Amino- or 2 : 4-diamino-6-methylpyrimidine and (**I**) give 2-*picramido*-6-*methyl*-, m.p. 166—167°, or 2-*picramido*-4-*amino*-6-*methyl*-*pyrimidine*, m.p. 195—196° [4-*acetate* (**II**), m.p. 235°], converted by boiling with PhOH–$PhNO_2$ into 4 : 6-*dinitro*-6′-*methyl*-, m.p. >300°, or 4 : 6-*dinitro*-4′-*amino*-6′-*methyl*-*pyrimidino*-(1′ : 2′-2 : 1)-*benziminazole*, m.p. >330° [*acetate*, m.p. 323—325°, by acetylation or from (**II**)], respectively. 6-Methylpyrimidine (**III**) and $NaNH_2$–Bu^aBr give 6-amylpyrimidine, b.p. 105—130°/0·01 mm., 135—138°/0·03 mm. (*picrate*, m.p. 126—128°). (**III**) and CH_2PhCl–$NaNH_2$ afford 6-(*dibenzylmethyl*)*pyrimidine*, b.p. 105—110°/0·01 mm. (*hydrochloride*, m.p. 259—260°; *aurichloride*, m.p. 198—200°), and a *compound*, $C_{24}H_{22}N_4$, b.p. 189—190°/0·01 mm., m.p. 120° (*picrate*, m.p. 153—155°), probably formed from 2 mols. of 6-(β-phenylethyl)pyrimidine. 6-Styrylpyrimidine is hydrogenated (Pd) to 6-(*β-phenylethyl*)-*pyrimidine*, m.p. 27—30° (*picrate*, m.p. 123—125°). 4-Hydroxy-2-benzyl-6-methylpyrimidine and $POCl_3$ at 120—130° give the corresponding 4-*Cl*-compound, m.p. 81—83°, converted by Zn–H_2O into 2-*benzyl*-6-*methylpyrimidine*, m.p. 36—37°, b.p. 135—140°/5 mm. (*picrate*, m.p. 126°; *hydrochloride*, m.p. 175—176°). $CH_2Ac{\cdot}CO{\cdot}CH_2Ph$–$CO(NH_2)_2$–HCl–EtOH afford 2-*hydroxy*-6-*benzyl*-, m.p. 61—63° [and a *substance*, $C_{12}H_{12}ON_2$, $+H_2O$, m.p. 167—169°, converted by boiling H_2O or aq. EtOH into (**III**)], and ($POCl_3$) 2-*chloro*-6-*benzyl*-4-*methylpyrimidine*, m.p. 27—28°, b.p. 170—175°/4 mm., and thence (Zn–H_2O) 6-*benzyl*-4-*methylpyrimidine*, b.p. 140—145°/4 mm. (picrate, m.p. 148°; hydrobromide, m.p. 151—152°). A. T. P.

Quinoline derivatives. VI. D. Das-Gupta and T. N. Ghosh (*J. Indian Chem. Soc.*, 1941, **18**, 120—122).—$[CO_2Et{\cdot}CH(CO{\cdot}NHPh)]_2CO$ with *m*- and *p*-$C_6H_4Me{\cdot}NH_2$ at 160—170° yields αα′-m-, m.p. 206—207° (which does not condense with aldehydes in AcOH), and -p-*tolylcarbamyl*-*acetonedicarboxylic acid dianilide*, m.p. 222—223°, which could not be converted into C_5H_5N derivatives. 2 : 4-Dihydroxy-3-carbethoxy- with NH_2Ph at 170° yields 2 : 4-*dihydroxy*-3-*phenylcarbamyl*-6-*methylpyridine*, m.p. 279—280°, converted by conc. H_2SO_4 at 100° into 2 : 2′-*dihydroxy*-6-*methylpyridino*-3 : 4-(3′ : 4′)-*quinolinedisulphonic acid* ($+H_2O$), m.p. >300° (*picrate*, turns brown at 217°, black >300°; Ac derivative uncrystallisable), unaffected by aq. NaOAc or boiling conc. HCl. A. Li.

Diquinolyls. VII. Formation of 2 : 3′-diquinolyl by action of selenium on quinoline. K. Ueda (*J. Pharm. Soc. Japan*, 1940, **60**, 210).—Quinoline with Se at 280—300° yields 2 : 3′-diquinolyl. A. Li.

Di*iso*quinolyls. I. Synthesis of 4 : 4′-di*iso*quinolyl. K. Ueda (*J. Pharm. Soc. Japan*, 1940, **60**, 210).—4-Bromo*iso*quinoline with N_2H_4,H_2O in EtOH–KOH in presence of Pd–$CaCO_3$ yields 4 : 4′-*diisoquinolyl*, m.p. 149°. A. Li.

Metallic triazine complexes. F. G. Mann (*Nature*, 1941, **147**, 778—779).—A discussion (cf. A., 1941, **II**, 93). Hexacovalent Pd^{II} compounds have been described previously (cf. A., 1929, 678). L. S. T.

Chemotherapy of bacterial infections. IV. Synthesis of *N′*-sulphonamide-substituted heterocyclic derivatives of sulphanilamide. K. Ganapathi (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 386—389).—The following compounds have been obtained by standard methods: *sulphanilyl*-, m.p. 188—189°, *acetylsulphanilyl*-, m.p. 266°, N^4-*sulphanilylsulphanilyl*-, m.p. 155—160°, and N^4-*acetylsulphanilylsulphanilyl*-, m.p. 143—145° (decomp.), *-guanidine*; 4-N^1-*sulphanilamidouracil*; 5-N^1-*sulphanilamidobarbituric acid*; 2-N^1-*sulphanilamido*-, m.p. 216—218°, and 2-N^1-*sulphanilamido*-5-*methyl*-, m.p. 190—192°, -1 : 3 : 4-*thiodiazole*; 2-N^1-*sulphanilamido*-, m.p. 240—242°, 2-N^1-*sulphanilamido*-4-*methyl*-, m.p. 236—238°, 2-N^1-*sulphanilamido*-4 : 6-*dimethyl*-, m.p. 235—240°, and 2-N^1-*sulphanilamido*-4 : 6 : 6-*trimethyldihydro*-, m.p. 230—232°, *-pyrimidine*; 7-N^1-*sulphanilamidoalloxazine*. The group $NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NR$ is essential for therapeutic activity, the degree and range of which are governed by the nature of R present at the sulphonamide radical. Of R tried, only the heterocyclic compounds the ring structures of which are present in products of vital biochemical functions (as vitamins or co-enzymes) yield sulphanilamide derivatives of outstanding val. Apparently some sp. spatial configuration of the whole mol. is essential for intense therapeutic activity. H. W.

Cobalt compounds of protoporphyrin. H. F. Holden (*Australasian J. Exp. Biol.*, 1941, **19**, 89—92).—The visible and ultraviolet spectra of cobalti- and cobalto-protoporphyrins and their compounds with globin, KCN, and glyoxaline are described. D. M. N.

Pyrrole series. V. Reinvestigation of the configuration of hæmin. A. H. Corwin and R. H. Krieble (*J. Amer. Chem. Soc.*, 1941, **63**, 1829—1834; cf. A., 1940, II, 193).—Rigid proof is provided of the structure of "natural" deuteroporphyrin (**I**) (Fischer *et al.*, A., 1928, 1385), mainly by alternative unambiguous synthesis of intermediates. Et_2 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate and aq. KOH at 160° give 95% of 2 : 4-dimethylpyrrole (**II**), b.p. 72°/25 mm., unstable in air. Addition of $COEt{\cdot}CH_2{\cdot}NH_2,HCl$ (prep. *in situ* from $COEt{\cdot}CH{:}N{\cdot}OH$ by mossy Sn–$SnCl_2$–HCl improved) and 1% NaOH (to maintain p_H 6) to $CO_2Et{\cdot}C(ONa){:}CH{\cdot}CO_2Et$ in H_2O at 85° gives 65% of 4-carbethoxy-2 : 3-dimethylpyrrole-5-carboxylic acid, m.p. 210° (decomp.), converted as above into 2 : 3-dimethylpyrrole (**III**), b.p. 72°/25 mm., more stable than (**II**). Passing HCl into (*a*) 5-formyl-2 : 4-dimethylpyrrole (modified prep.; 75% yield), m.p. 91°, and (**III**), or (*b*) 5-formyl-2 : 3-dimethylpyrrole (**IV**), m.p. 127·5—128°, and (**II**) in abs. EtOH gives 95% of the hydrochloride, decomp. 222°, converted (83%) by a little aq. NH_3 into 3 : 5 : 4′ : 5′-dipyrrylmethene (**V**), m.p. 82—83°, unstable. Fischer's m.p. 115° for (**V**) is erroneous, attempts to repeat his experiments exactly giving, in one experiment, only a similar, but mixed, product. HCl, 90% HCO_2H, and (**II**) in EtOH give under defined conditions 50% of the hydrochloride (**VI**), red and blue forms, decomp. 226°, converted as above into 3 : 5 : 3′ : 5′-tetramethyldipyrrylmethene (**VII**), m.p. 116—118°. (**III**), (**IV**), and conc. HCl in EtOH give the hydrochloride (80%), decomp. 212°, of 4 : 5 : 4′ : 5′-tetramethyldipyrrylmethene (**VIII**), m.p. 116°. HCO_2H and (**III**) give only NH_4Cl. (**V**), (**VII**), and (**VIII**) give depressions of m.p. when mixed. Addition of Fe powder to deuterohæmin in HCl–AcOH, pptn. of the porphyrin by H_2O, boiling with dry HCl–AcOH, and purification by chromatography gives "natural" deuteroporphyrin Me_2 ester (**IX**), m.p. 224·5°. Br and (**VI**) in boiling CCl_4–$CHCl_3$ give 4 : 4′-dibromo-3 : 5 : 3′ : 5′-tetramethyldipyrrylmethene hydrobromide (**X**) (>83%). Prep. of 5 : 5′-dibromo-4 : 4′-dimethyldipyrrylmethene-3 : 3′-dipropionic acid hydrobromide (**XI**) from 5-carbethoxy-2 : 4-dimethylpyrrole-3-acrylic acid (hydrogenation: $PdCl_2$–C; aq. NaOH) by way of the 3-propionic acid, m.p. 153°, the 2-bromomethyl-3-propionic acid, and 5 : 5′-dicarboxy-4 : 4′-dimethyldipyrrylmethane-3 : 3′-dipropionic acid is improved. Heating (**X**), (**XI**), and BzOH at 180—182°, esterification of the product, and chromatography gives *deuteroporphyrin* XIII Me_2 ester, m.p. 243—243·5° [depression of m.p. with (**IX**)]. Similarly, but including debromination by hydrogenation (Busch catalyst; C_6H_6), 4 : 3′-dibromo-3 : 5 : 4′ : 5′-tetramethyldipyrrylmethene hydrobromide, (**XI**), and BzOH give deuteroporphyrin IX Me_2 ester, m.p. 223·5—224°, identical with "natural" (**IX**). R. S. C.

Absorption spectra of *ms*-tetraphenylporphine and its metal complex salts.—See A., 1941, **I**, 397.

Phenolic invert soaps. J. B. Niederl and F. A. Abbruscato (*J. Amer. Chem. Soc.*, 1941, **63**, 2024).—Treatment of *p*-$CH_2Bu^{\gamma}\cdot CMe_2\cdot C_6H_3\cdot OH$ with 30% CH_2O and NHR_2 in MeOH at room temp. and then with MeI gives 4-2′-*hydroxy*-5′-*aαγγ-tetramethyl*-n-*butylbenzylmorpholine*, m.p. 44—45° (*methiodide*, m.p. 176—177·5°), 1-2′-*hydroxy*-5′-*aαγγ-tetramethyl*-n-*butylbenzylpiperidine*, m.p. 92—93° (*methiodide*, m.p. 162—163·5°), 2-*hydroxy*-5-*aαγγ-tetramethyl*-n-*butylbenzyldi-ethyl*-, m.p. 124—125°, -n-*propyl*-, m.p. 135—136·6°, and -n-*butyl*-*ammonium iodide*, m.p. 132—133°. R. S. C.

Synthesis of 3 : 5-diamino-4-morpholinopyridine. E. Ochiai and Y. Ito (*J. Pharm. Soc. Japan*, 1941, **61**, 53—54).—4-Hydroxypyridine is converted by fuming HNO_3 and fuming H_2SO_4 at 140—145° into 3 : 5-*dinitro*-4-*hydroxypyridine*, decomp. 325°, transformed by the successive actions of $POCl_3$ + PCl_5 at 140° and morpholine in boiling abs. EtOH into 3 : 5-*dinitro*-, m.p. 163—164°, reduced (Pd–C in HCl–MeOH) to 3 : 5-*diamino*-4-*morpholinopyridine*, m.p. 231° (*picrate*, m.p. 213°; *Ac*$_2$ derivative, m.p. 216°). H. W.

Thiazolines.—See B., 1941, **II**, 335.

Polarisation in heterocyclic rings with aromatic character. XII. Polarisation in the thiazole ring. III. F. Nagasawa (*J. Pharm. Soc. Japan*, 1940, **60**, 219—224).—The activity of the $C_{(4)}$ like that of the $C_{(5)}$ position towards electrophilic reagents is slight; it is increased by the presence of substituents with +*M* or +*E* effect at $C_{(2)}$ but not to the extent observed with the activity of $C_{(5)}$. Treatment of 2-*amino*-5-*methylthiazole* (**I**), b.p. 80°/0·01 mm., m.p. 95—96·5°, with H_2SO_4 + HNO_3 causes decomp. without production of NO_2-derivatives. Nitration [H_2SO_4 (*d* 1·84) + HNO_3 (*d* 1·5)] of 2-*acetamido*-5-*methylthiazole*, m.p. 224°, at 0° gives small amounts of a NO_2-derivative, m.p. 249° (*picrate*), and much resin. The respective thiazoles are converted by fuming H_2SO_4 (20% SO_3) and HNO_3 at 160° into 4-*nitro*-2 : 5-*dimethyl*-, m.p. 56·5°, *nitro*-4-*methyl*-, m.p. 57·5°, and 5-*nitro*-2 : 4-*dimethyl*-, b.p. 65°/0·07 mm., -*thiazole*. 2 : 5-Dimethylthiazole is unaffected by fuming H_2SO_4 (20% SO_3) at 100° or 150° but is transformed by prolonged action of the acid at 200° into 2 : 5-*dimethylthiazole*-4-*sulphonic acid*, decomp. 284° [*Ba* salt (+1H_2O), decomp. 353°], in relatively poor yield. 2-*Hydroxy*-5-*methylthiazole*, m.p. 139—141·5°, reacts with fuming H_2SO_4 (20% SO_3) at room temp., 60°, and 100° (best at 60°) giving the non-cryst. -4-*sulphonic acid* [*Ba* salt (+1H_2O)] but reaction occurs less readily than with the -4-Me compound. (**I**) and fuming H_2SO_4 (20% SO_3) at 60° or 100°, but not at 1°, afford a *monosulphonic* acid, decomp. 292° [*Ba* salt (+1H_2O)], which could not be diazotised and is re-converted into (**I**) by conc. HCl at 135°. 2-*Piperidino*-5-*methylthiazole* (**II**), b.p. 128°/4 mm., m.p. 35° (*picrate*, m.p. 144°), is transformed by fuming H_2SO_4 (20% SO_3) at room temp. or 60° into the -4-*sulphonic* acid, decomp. 273° (*Ba* salt). Under similar conditions 2-*piperidino*-4-*methylthiazole* (**III**), b.p. 102—104°/4 mm., m.p. 36° (*picrate*, m.p. 153°; *perchlorate*, m.p. 126·5°), gives 2-*sulphon*-ω-*hydroxyamylamido*-4-*methylthiazole*-5-*sulphonic acid* (*Ba* salt). 2-Hydroxy-5-methylthiazole decolorises Br in $CHCl_3$ and evolves HBr at room temp. but the product is too unstable to permit its isolation; under like conditions (**I**) does not decolorise Br and (**II**) does not yield a Br-derivative, whereas (**III**) is transformed into 5-*bromo*-2-*piperidino*-4-*methylthiazole*, m.p. 39·5° (*perchlorate*, m.p. 158°). 2-Acetamido-4-methylthiazole, H_2SO_4 (*d* 1·84), and HNO_3 (*d* 1·5) give 5-*nitro*-2-*acetamido*-4-*methylthiazole*, decomp. 224°. H. W.

Molecular compounds in the sulphonamide series. II. S. Kuroyanagi and H. Kawai (*J. Pharm. Soc. Japan*, 1940, **60**, 183—184).—M.p. and f.p. curves for combinations of (*a*) *p*-$NH_2\cdot C_6H_4\cdot SO_2\cdot NH_2$ (**I**), *p*-$NH_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_6H_4\cdot SO_2\cdot NMe_2$-*p*, or 2-sulphanilamidopyridine (**II**), and (*b*) 5 : 5-diethylbarbituric acid, dimethylaminoantipyrine (**III**), or 2-phenylquinoline-4-carboxylic acid (**IV**) show that only two combinations, viz., (**I**) (1 mol.) + (**IV**) (2 mols.), and (**II**) (1 mol.) + (**III**) (1 mol.), gave evidence of formation of mol. compounds. Thermal analysis of the systems 2-sulphanilamido-6-methylpyridine and (**III**) or *p*-$NO_2\cdot C_6H_4\cdot OH$ (**V**), and 2-sulphanilamido-4-methylthiazole and (**V**), shows that no mol. compound is formed. A. T. P.

Preparation of γ-diethylaminopropyl derivatives of 1-aminobenzthiazole. K. Tsuda, S. Sakamoto, H. Matsuda, and T. Kanno (*J. Pharm. Soc. Japan*, 1940, **60**, 184—189).—1-Acetamidobenzthiazole (**I**) (1 mol.) in NaOEt (1 mol.)–EtOH [or the K salt of (**I**) in EtOH] and $Br\cdot[CH_2]_3\cdot NEt_2$, HBr (**II**) (1·3 mols.) in NaOEt (1·3 mols.)–EtOH at 100° (bath) afford 1-N-*acetyl*-γ-*diethylaminopropylaminobenzthiazole*, b.p. 185—187°/0·03 mm. (*dipicrate*, m.p. 158°), hydrolysed by 10% aq. HCl at 100° (bath) to γ-*diethylaminopropylaminobenzthiazole*, b.p. 200—210°/0·01 mm. [*dipicrate*, m.p. 197° (or +$COMe_2$, m.p. 168°); meconate, m.p. 179° (decomp.)], also obtained from 1-chlorobenzthiazole and $NH_2\cdot[CH_2]_3\cdot NEt_2$ at 100°. 1-Aminobenzthiazole (**III**) or (**I**) and (**II**) at 130° afford 1-*imino*-2-γ-*diethylaminopropyl*-1 : 2-*dihydrobenzthiazole*, b.p. 170—180°/0·03 mm. [*dipicrate*, m.p. 192° (+H_2O); *meconate*, m.p. 217° (decomp.)] [*acetimino*-derivative, m.p. 57° (*dipicrate*, m.p. 145°)]. The following are prepared: 3-*methoxy*-, m.p. 146° (Ac derivative, m.p. 213°), and 4-*chloro*-1-*aminobenzthiazole*, m.p. 205° (*Ac* derivative, m.p. 291°); 5-*chloro*-, m.p. 62° [*dipicrate*, m.p. 188°; *meconate*, m.p. 165° (decomp.); *Ac* derivative, m.p. 107°], 5-ethoxy- [*meconate*, m.p. 210° (decomp.); *Ac* derivative, m.p. 96°], 5-amino- [*meconate*, m.p. 203° (+1·5$C_7H_4O_7$); *Ac* derivative, m.p. 202°], 3-*chloro*- [*dipicrate*, m.p. 170°; *meconate* (+3H_2O), m.p. 113° (decomp.); *Ac* derivative, b.p. 230°/0·01 mm. (*dipicrate*, m.p. 162°)], and 1-γ-*diethylaminopropylamino*-3-*methoxybenzthiazole*, b.p. 200°/0·01 mm. [*dipicrate*, m.p. 202°; *meconate*, m.p. 154—155° (decomp.); *Ac* derivative, b.p. 210°/0·01 mm. (*dipicrate*, m.p. 153°)]; 5-*nitro*-1-N-*acetyl*-γ-*diethylaminopropylaminobenzthiazole*, m.p. 129°; 5-chloro-, b.p. 190—200°/0·05 mm. [*dipicrate*, m.p. 143° (decomp.); meconate, m.p. 232° (decomp.)], 5-methoxy- [*meconate*, m.p. 217—218° (decomp.)], 3-chloro-, b.p. 200°/0·1 mm. [*dipicrate*, m.p. 190°; *meconate*, m.p. 230° (decomp.)], and 3-*methoxy*-1-*imino*-2-γ-*diethylaminopropylbenzthiazoline*, b.p. 170—200°/0·05 mm. (*dipicrate*, m.p. 196—198°; meconate). (**III**) and $O\cdot CH_2\cdot CH\cdot CH_2\cdot NEt_2$ yield 1-γ-*diethylamino*-β-*hydroxypropyl*)*aminobenzthiazole*, b.p. 230—250°/0·01 mm. (*dipicrate*, m.p. 189°), also obtained from 1-chlorobenzthiazole and $NH_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NEt_2$. 2-Acetamido-4-methylthiazole is converted (K salt–MeI; reflux) into the N-*Me* derivative, m.p. 110°, or (MeI at 100°) into 2-*acetimino*-3 : 4-*dimethylthiazole*, m.p. 115° (+H_2O, m.p. 51°). A. T. P.

Heterocyclic sulphonamides. U. P. Basu and S. J. Das-Gupta (*J. Indian Chem. Soc.*, 1941, **18**, 167—168).—2-Chloro-*cyclo*hexanone with $CS(NH_2)_2$ in boiling EtOH yields 2-amino-3 : 4-tetrahydrobenzthiazole (*hydrochloride*, m.p. 243—244°), which with *p*-$NHAc\cdot C_6H_4\cdot SO_2Cl$ (**I**) in C_5H_5N at room temp. yields the *Ac* derivative, m.p. 180° (indef.), of 2-*sulphanilamido*-3 : 4-*tetrahydrobenzthiazole* (**II**), m.p. 150—154° (indef.). 4-Methylthiazole with (**I**) in EtOAc at room temp. and hydrolysis (5% HCl in 50% EtOH at 100°) of the product yields 2-sulphanilamido-4-methylthiazole (Fosbinder *et al.*, A., 1939, II, 525). (**I**) and 4-sulphanilamido-1-phenyl-2 : 3-dimethyl-5-pyrazolone (Roblin *et al.*, A., 1940, II, 359) show no activity against pneumococcal (type I) infections in white mice. A. Li.

Synthesis of methoxy-γ-diethylaminopropyl derivatives of benzthiazole and benziminazole. E. Ochiai and M. Katada (*J. Pharm. Soc. Japan*, 1940, **60**, 211—216).—2-*Amino*-5-, m.p. 154° (*picrate*, decomp. 230—255°) [prepared by treating diazotised 3 : 4 : 1-$NO_2\cdot C_6H_3(NH_2)\cdot OMe$ with KCNS and $Cu_2(CNS)_2$, and reducing ($SnCl_2$ + HCl) the resulting 3-*nitro*-4-*thiocyanoanisole*, m.p. 126°], and -6-methoxy-, m.p. 158° [from *p*-$OMe\cdot C_6H_4\cdot NH\cdot CS\cdot NH_2$ (1 mol.) and Br (3 atoms) in $CHCl_3$ at 50°; cf. Dyson *et al.*, A., 1927, 680; different reaction conditions yield a Br-containing product, decomp. 222°], and 4-amino-6-methoxy-benzthiazole (prepared by the method of Fox *et al.*, A., 1939, II, 524) yield *Ac* derivatives, m.p. 223° (*K* salt, decomp. 265°), 226°, and 157—158°. The Na or K salts of which with $NEt_2\cdot[CH_2]_3\cdot Br$ in EtOH yield the *Ac* derivatives, b.p. —, 195—200° (bath temp.)/0·6 mm. (*picrate*, m.p. 188°), and 195—205° (bath temp.)/0·02 mm. (*perchlorate*, decomp. 186°), respectively, of 2-γ-*diethylaminopropylamino*-5-, b.p. 195—200° (bath temp.)/0·9 mm. (*perchlorate*, decomp. 244—245°), and -6-*methoxy*-, b.p. 200—205° (bath temp.)/0·7 mm. (*picrate*, decomp. 198°; *perchlorate*, decomp. 193°), and 4-γ-*diethylaminopropylamino*-6-*methoxy*-*benzthiazole*, b.p. 215—220° (bath temp.)/0·8 mm. (*picrate*, decomp. 141°). 1 : 3 : 4-$OMe\cdot C_6H_3(NH_2)_2$,2HCl with HCO_2H yields 6-*methoxybenziminazole*, m.p. 123° [*picrate*, m.p. 191°; 1-$NEt_2\cdot[CH_2]_3$

derivative (NEt_2·$[CH_2]_3$·Br in EtOH–NaOEt), b.p. 195—200° (bath temp.)/0·2 mm. (*picrate*, m.p. 174°)], nitration (room temp.) of which yields 5-nitro-, m.p. 244° (*nitrate*, decomp. 204°), reduced (Pd) to 5-amino-6-methoxybenziminazole {*Ac*, m.p. 210°, and NEt_2·$[CH_2]_3$ derivative, b.p. 135—140° (bath temp.)/0·06 mm. (*picrate*, decomp. 206°)}. A. Li.

Sulphanilamides derived from pyridine, quinoline, and thiazole.—See B., 1941, III, 245.

Synthesis of heterocyclic derivatives of diaryl sulphones. I. E. Ochiai and T. Takubo (*J. Pharm. Soc. Japan*, 1941, **61**, 6—7).—2-Chloro-4-methylthiazole with *p*-NO_2·C_6H_4·OH or 2-thiol-4-methylthiazole (**I**) and Zn in anhyd. C_5H_5N at 120—130° gives p-NO_2·C_6H_4·*4-methyl-2-thiazolyl*, m.p. 54°, and *di-4-methyl-2-thiazolyl sulphide*, b.p. 134—135°/16 mm. (*picrate*, m.p. 136°), oxidised by 30% H_2O_2 in AcOH at room temp. to the corresponding *sulphones*, m.p. 171° and 125°, respectively. 2-Chloropyridine and (**I**) similarly yield *2-pyridyl 4-methyl-2-thiazolyl sulphide*, b.p. 166—168°/0·05 mm. (*picrate*, m.p. 118°), and *sulphone*, m.p. 121°. R. S. C.

5-Ethinylruban-5-ol and related compounds. G. R. Clemo and E. Hoggarth (*J.C.S.*, 1941, 476—477).—Condensation of 5-ketoruban with C_2H_2 in presence of K in *tert.*-C_5H_{11}·OH gives *5-ethinylruban-5-ol*, m.p. 213°, which is reduced (Pt–H_2) to 5-ethylruban-5-ol. 5-Keto-6 : 9-rubanene with C_2H_2 affords a *compound*, $C_{19}H_{18}ON_2$, m.p. 238°, reduced to the substance obtained by the action of MgEtI on the ketone. Similarly 3-ketoquinuclidine (**I**) and C_2H_2 yield *3-hydroxy-3-ethinylquinuclidine*, m.p. 159—160°, reduced to the *-3-Et* compound, b.p. 98—100°/1 mm. (*picrate*, m.p. 178°), also formed from MgEtI and (**I**). F. R. S.

Constitution of yohimbine. M. J. S. Dewar and F. E. King (*Nature*, 1941, **148**, 25).—Distillation of yohimbic acid with Cu and CuO instead of alkali improves Hahn's prep. of yohimbol (A., 1928, 432). The identity observed between the H_2SO_4 colour transformations of this carboxyl-free *sec.* alcohol and of yohimbine invalidates the evidence which places the CO_2Me at $C_{(f)}$ (A., 1941, II, 176). The structure now proposed has CO_2Me at $C_{(16)}$ and OH at $C_{(19)}$. L. S. T.

Azo compounds of morphine. I. A. C. Roy (*J. Indian Chem. Soc.*, 1941, **18**, 29—32).—When morphine is coupled with ArN_2Cl to give azo dyes, the pharmacological activity is modified but not destroyed. Azo dyes thus prepared are benzene-, m.p. 175° (decomp.) (cryst.); p-*methyl-*, m.p. 210° (decomp.) (amorphous), 2 : 4-*dimethyl-* (this and the following do not melt at 300° and are amorphous), p-*chloro-*, 2 : 4 : 6-*tribromo-*, p-*hydroxy-*, o-*methoxy-*, and o-, m-, and p-*nitrobenzene-azomorphine*; α-*naphthaleneazomorphine*; *diphenyl-4 : 4'-bisazomorphine*. A. T. P.

Alkaloids of *Rauwolfia canescens* (Linn.). I. (Miss) A. Mookerjee (*J. Indian Chem. Soc.*, 1941, **18**, 33—39).—The air-dried leaves of *R. canescens* are extracted with EtOH (+0·1% AcOH) at room temp., the extract is conc., added to H_2O, extracted with Et_2O, and the aq. solution made alkaline with NH_3 and extracted with Et_2O, and the alkaloid pptd. as the *oxalate*, m.p. 245—246° (decomp.) (+$2H_2O$, lost at 125—130° over P_2O_5), which is decomposed by aq. NH_3 to "*rauwolscine*" (**I**), $C_{21}H_{26}O_3N_2$, m.p. 231—232° (decomp.), $[\alpha]_D^{30}$ −40° in EtOH (contains CO_2Me) [*hydrochloride*, m.p. 278—280° (decomp.), $[\alpha]_D^{30}$ +74° in H_2O; *nitrate*, m.p. 257—258° (decomp.); *sulphate*, m.p. 256—257° (decomp.); *platinichloride*, m.p. 255—257° (decomp.); *picrate*, m.p. 208° (decomp.) (+2EtOH)], which with conc. NH_3 at room temp. in a closed vessel affords *rauwolscinic acid*, m.p. 262—264° (decomp.) [+H_2O, lost at 120—125° (P_2O_5)], reconverted into (**I**) by HCl–MeOH. (**I**) shows similar colour reactions to those of yohimbine, with which it is not identical. Some photomicrographs are shown. A. T. P.

Alkaloids of *Stemona tuberosa*, Loureiro. III. Tuberostemonine. H. Kondo, K. Suzuki, and M. Satomi (*J. Pharm. Soc. Japan*, 1940, **60**, 149—157; cf. A., 1940, II, 237).—Tuberostemonine (**I**) in MeOH or 2N-HCl is slowly hydrogenated in presence of a very large proportion of PtO_2 to hydrotuberostemonine (**II**), m.p. 133° (hydrochloride, m.p. 281°); the "isomeride," m.p. 118—120° (cf. Schild, A., 1936, 350), is separated chromatographically into (**I**) and (**II**). After treatment with Ag_2O (**II**) does not give Ehrlich's reaction for pyrrole; it does not react with MeI although it behaves as a weak base towards mineral acid. Tuberostemonine methohydroxide passes at 145°/vac. into *hydroxy-N-methyltuberostemonine* (**III**), $C_{23}H_{37}O_5N$, m.p. 123—125° (*perchlorate*, m.p. 217°), which is stable at 130°/vac. Like its *Ac* derivative, decomp. 213°, (**III**) does not react with MeI in MeOH. (**III**) does not appear to yield an oxime. Me_2SO_4 transforms (**III**) at 120° into an amorphous substance characterised as the *perchlorate*, $C_{23}H_{35}O_5N,HClO_4$, m.p. 210°, with a small proportion of a cryst. *material*, $C_{23}H_{37}O_5N,Me_2SO_4$, m.p. 245°. (**III**) and CNBr in C_6H_6 at room temp. yield an *adduct*, $C_{23}H_{37}O_5N,CNBr$, m.p. 232° (decomp.), which is not affected by boiling 2N-KOH–EtOH or by 20% H_2SO_4 at 120°. (**III**) is dehalogenated by Ag_2O and then transformed by 30% H_2SO_4 or HCl into the *anhydro-base*, $C_{23}H_{36}O_5N_2$, m.p. 210°, which with 30% HCl at 100° gives the *chlorocyanide*, $C_{24}H_{35}O_4N_2Cl$, m.p. 160°. Hydrolysis of (**I**) by 0·5N-KOH–EtOH and treatment of the neutralised solution with CH_2N_2 leads only to the re-formation of (**I**). Similarly successive treatment of (**I**) with KOH–EtOH, Me_2SO_4, and KI gives only tuberostemonine methiodide, m.p. 236—238°, also obtained from K tuberostemonate and MeI. (**I**) does not appear to be changed by Na and EtOH but is converted by Na and boiling *iso*-C_5H_{11}·OH into an amorphous base. (**I**) does not react with solid KOH and *iso*-C_5H_{11}·OH at 100—200°. H. W.

VI.—ORGANO-METALLIC COMPOUNDS.

Asymmetrical analogues of cacodyl oxide. G. Kamai and V. M. Zoroastrova (*J. Gen. Chem. Russ.*, 1940, **10**, 1568—1572).—$AsEtI_2$ and $Pr^{\beta}Br$ with 5N-NaOH in 55% EtOH yield *ethylisopropyliodoarsine*, b.p. 87—88°/13 mm. *Benzylethyliodoarsine*, b.p. 169—170°/15 mm., is prepared similarly from $AsEtI_2$ and CH_2PhBr. AsRR'I and 10N-NaOH at room temp. yield oxides of the type $(AsRR')_2O$ (R = Me, R' = Et; R = *Et*, R' = *Pr*$^{\beta}$, b.p. 130—132°/17 mm.; R = *Me*, R' = *Ph*, b.p. 202—203°/15—16 mm.; R = *Et*, R' = *Ph*, b.p. 189°/5 mm.; R = *Et*, R' = CH_2Ph, b.p. 174—175°/16 mm.; R = Ph, R' = *p*-tolyl). $(AsPhMe)_2O$ is oxidised by atm. O_2 to phenylmethylarsinic acid, m.p. 178—179°, which with CH_2Cl·CO_2Na yields *phenylmethyloxarsylacetic acid*, converted by H_2S into *phenylmethylthioarsylacetic acid* [*phenyl(carboxymethyl)methylarsine sulphide*], m.p. 132—133°. R. T.

Steric hindrance in Grignard reaction. I. Reaction of magnesium mesityl bromide with ethyl formate and acetate. I. I. Lapkin, V. S. Schklaev, and T. I. Schklaeva (*J. Gen. Chem. Russ.*, 1940, **10**, 1449—1452).—Mg mesityl bromide (**I**) and HCO_2Et in Et_2O react with difficulty at the b.p., yielding mesitol and dimesitylmethane. (**I**) does not react with EtOAc in Et_2O; in PhMe it reacts only very slowly (30 hr. at the b.p.), yielding mesityl acetate and αα-dimesitylethyl acetate. R. T.

Chemotherapy of bacterial infections. II. Chemistry of some organo-selenium compounds related to sulphanilamides. P. L. N. Rao (*J. Indian Chem. Soc.*, 1941, **18**, 1—6; cf. A., 1940, II, 274).—*p*-NHAc·C_6H_4·SeCN (1 part) refluxed with 2·5N-KOH–EtOH (5 parts for 6 hr. or 1·7 parts for ½ hr.) gives p-*amino-* (**II**), m.p. 76—78°, or *-acetamido-selenophenol* (**III**), m.p. 160—165°, respectively. (**I**)–$(NH_4)_2S$ yield (**III**) and (*p*-NHAc·C_6H_4)$_2$Se. (**III**) is oxidised (dil. H_2O_2) to *di*-p-*acetamidophenyl diselenide*, m.p. 204—206° (softens from 180—182°), and (**II**) (prepared as above but not isolated) is oxidised by atm. O_2 or H_2O_2 to (*p*-NH_2·C_6H_4)$_2Se_2$ [*sulphate*, m.p. 210—215° (decomp.); *Bz*$_2$ derivative (**IV**), m.p. 265—267° (decomp.); *di-hexoyl*, m.p. 175—177°, and *-valeroyl* derivative, m.p. 172—173°]. *p*-NO_2·C_6H_4·SeO_2H, neutralised with NH_3, is oxidised by aq. $KMnO_4$ to *K 4-nitrophenylselenonate* (anhyd. or +H_2O, gradually lost at room temp.). (**IV**) and HNO_3 (*d* 1·4) at −6° to −3° afford *4-benzamidophenylseleninic acid*, m.p. 186° (decomp.) [hydrolysed to the 4-NH_2-compound (*Ba* salt)], and thence *K 4-benzamidophenylselenonate*. *Ag 4-acetamidophenylselenonate* is prepared in an analogous manner. *p*-NO_2·C_6H_4·SeCN, *p*-C_6H_4Br·NO_2, and aq. K_2CO_3–EtOH (refluxed for 2 days) yield (*p*-NO_2·C_6H_4)$_2$Se (**V**), new m.p. 175°, reduced to 4 : 4'-*diaminodiphenyl selenide*, m.p. 115—117°, which is also obtained by hydrolysis of the corresponding Ac_2 derivative. *p*-$C_6H_4Br(Cl)$·NO_2 and Na_2Se–Se–EtOH give (*p*-NO_2·C_6H_4)$_2Se_2$ and (**V**) (cf. Baker *et al.*, A., 1930, 1302). (**I**) and Br–$CHCl_3$ afford *4-acetamidophenylselenotribromide*, m.p. 130—132° (decomp.) (softens at 100°), which loses 2 Br in vac. (1 week) to give the *-selenobromide*

(boiling H_2O yields a substance, m.p. 168—169°). *p*-$NO_2{\cdot}C_6H_4{\cdot}SeO_2K$ and PCl_5 afford *p*-$NO_2{\cdot}C_6H_4{\cdot}SeCl$, converted by ice-$H_2O$ or aq. NH_3 into (*p*-$NO_2{\cdot}C_6H_4)_2Se_2$ and *p*-$NO_2{\cdot}C_6H_4{\cdot}SeO_2H$. A. T. P.

VII.—PROTEINS.

Molecular structure of protein fibres. D. J. Lloyd (*J. Soc. Dyers and Col.*, 1941, **57**, 281—287).—Proteins are classified into silk fibroin, myosin–keratin, and collagen types. Their general properties are discussed, special emphasis being laid on the sorption of H_2O and swelling. C. S. W.

Nature of the intramolecular fold in α-keratin and α-myosin. W. T. Astbury and F. O. Bell (*Nature*, 1941, **147**, 696—699).—A basis for an intramol. fold in α-keratin and α-myosin is proposed, illustrated, and discussed. L. S. T.

Action of formaldehyde on gluten [gelatin?]. A. S. Schpitalski, E. A. Emelianova, and S. B. Faerman (*J. Appl. Chem. Russ.*, 1940, **13**, 1642—1648).—The effect of aq. CH_2O on aq. gelatin (**I**) varies according to the concn. of (**I**). When this is low the η increases, and gelation is prevented, whilst when it is high the opposite effects are produced. However, the dimensions of the (**I**) mols. appear to increase in all cases. CH_2O has little effect on hydrolysed (**I**). R. T.

Formation of humins during acid hydrolysis of proteins. V. A. Kaschirskich (*J. Gen. Chem. Russ.*, 1940, **10**, 1495—1500).—Insol. residues formed during hydrolysis of proteins (caseinogen) or NH_2-acids (glycine, alanine, crystine, glutamic acid, tyrosine, tryptophan) in presence of carbohydrates (glucose, fructose, lactose, galactose, arabinose, cellulose) by means of 20% HCl are supposed to originate from condensation of reactive furan compounds derived from the carbohydrates with NH_2-acids, or with each other, to yield nitrogenous or N-free humins, respectively. R. T.

Acyl and sulphonyl derivatives of proteins.—See B., 1941, II, 324.

Humin formation during protein hydrolysis.—See A., 1941, III, 948.

Carrier weights of conjugated proteins. E. E. Broda and C. F. Goodeve (*Nature*, 1941, **148**, 200—201).—Carrier wts., *i.e.*, the no. of g. of protein carrying 1 g.-equiv. of prosthetic group, are tabulated for numerous conjugated proteins. The data show that the Svedberg unit is the lower limit of the carrier wts., and that all sufficiently well-defined compounds have carrier wts. close to simple multiples of the unit. L. S. T.

VIII.—ANALYSIS.

Distilling column head.—See A., 1941, I, 391.

Continuous water remover.—See A., 1941, I, 392.

Simultaneous micro-determination of elements in organic compounds containing alkali. H. Agematsu (*J. Pharm. Soc. Japan*, 1940, **60**, 233—235).—C and H are determined essentially according to Pregl. Na compounds (3—5 mg.) are weighed into a Pt boat and covered with 2—3 times the amount of dry Cr_2O_3. With K salts 1—2 mg. of Cr_2O_3 suffices and an excess must be carefully avoided. The boat is heated gently with a moving burner until the contents are melted and then very strongly after carbonisation is complete. The residue is treated with H_2O and unchanged Cr_2O_3 is removed by an asbestos filter. CrO_4'' is determined in the filtrate gravimetrically as $PbCrO_4$ or iodometrically. N can be determined simultaneously. With explosive substances an addition of CuO is necessary. The process is not applicable in the presence of halogen or S because the metals produce very stable alkali halides and sulphates. H. W.

Micro-determination of nitrogen by oxidative digestion. C. N. B. Rao, M. V. L. Rao, and M. S. Ramaswamy (*Current Sci.*, 1941, **10**, 261—262).—An aq. suspension (1 c.c.) of the material is treated with conc. H_2SO_4 and HgO (~50 mg.) and to the boiling solution 100% chromic acid (0·2—0·3 c.c.) is added. After 5 min. the solution is diluted with H_2O (5—10 c.c.), decolorised with Na_2SO_3, and boiled after adding Zn dust (~10—20 mg.). The NH_3 is distilled from the solution which has been rendered alkaline and determined titrimetrically (colorimetrically when the NH_3 content is <10 μg.). J. L. D.

Adaptation of the micro-Kjeldahl method to determination of nitrogen in organic compounds containing nitro- and azo-groups. R. V. Bhat (*Proc. Indian Acad. Sci.*, 1941, **A**, **13**, 269—272).—A no. of NO_2- [*e.g.*, *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$, 3 : 5 : 1-$C_6H_3(NO_2)_2{\cdot}CO_2H$, etc.] and azo-compounds (*e.g.*, azo-dyes from Naphtol AS derivatives and diazotised Fast Red bases) are analysed correctly for N by the micro-Kjeldahl method, using pure cotton cellulose as reducing agent; the substance is heated with H_2SO_4 (*d* 1·84), K_2SO_4, and bleached cotton for ½ hr., $CuSO_4$ and H_2SeO_3 are then added, and heating is continued (1—1½ hr.), NH_3 being determined as usual. Details are given of the method, which is useful in estimating dyes on the fibre. A. T. P.

Determination of sulphur in organic compounds. Oxidation of sulphur of cystine and methionine, combination of Parr oxygen bomb and acidimetric benzidine method, and determination of small amounts of sulphur present as concontaminant in organic materials. T. P. Callan and G. Toennies (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 450—455).—A process for the oxidation of org. S compounds by $KMnO_4$–NaOH prior to S determination is described. Methionine gives no SO_4'' by this procedure, and other wet oxidation processes give variable and incomplete vals. A procedure is detailed in which the substance is burned in a bomb in compressed O_2, and the SO_4'' is determined acidimetrically as benzidine sulphate. The presence of Hg and NaCl, within certain limits, does not interfere in this method, which is accurate to a few hundredths %. J. D. R.

Micro-determination of sulphur. Modified bomb method. J. F. Alicino (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 506).—A modification of the Elek–Hill method (A., 1933, 1063) is described. The Na_2O_2 in the fusion mixture is decreased to 0·35 g., and 0·06 g. of $KClO_3$ is substituted for the sucrose + KNO_3. This reduction in quantity of the fusion mixture permits filtration of the $BaSO_4$ by filter-stick, minimises contamination of the $BaSO_4$ by co-pptn. and adsorption of salts, and eliminates the need for using reagents of special purity. Analyses of typical org. substances show the accuracy of the method. L. S. T.

Determination of iodine in organic compounds with the calorimetric bomb. I, II. B. Longo (*Atti R. Accad. Sci. Torino* [*Cl. Sci. fis. mat. nat.*], 1938, **73**, I, 428—430, 431—433; *Chem. Zentr.*, 1938, ii, 3843).—I. A modification of Garelli and Saladini's method for Cl and Br (cf. A., 1932, 1149) is extended to I. The KIO_3 formed in the bomb is reduced with N_2H_4 and the I determined by Volhard's method.

II. In presence of Cl or Br the solution from the bomb is treated with N_2H_4 and the halogens are determined in separate portions by Volhard's method, and by Gooch's method after treatment with HNO_2. A. J. E. W.

Determination of reactive hydrogen by Grignard's reagents in an atmosphere of carbon dioxide. A. P. Terentiev and K. D. Schtscherbakova (*J. Gen. Chem. Russ.*, 1940, **10**, 2041—2046).—The reactive H content of org. compounds is derived from the vol. of CH_4 evolved when the compound reacts with MgMeI in Et_2O in absence of atm. O_2. Apparatus for this method is described. R. T.

Determination and detection of dienes with conjugated ethylenic linkings. I. V. I. Esafov. **II.** V. I. Esafov and A. V. Schpadi (*J. Appl. Chem. Russ.*, 1941, **14**, 140—147, 148—150).—I. Kaufmann's iodometric method (A., 1937, II, 47) is not applicable to dienes with conjugated double linkings, owing to secondary polymerisation reactions. MacIlhiney's reaction is recommended for detection of dienes.

II. Non-conjugated polyenes react with Br in CCl_4 in the same way as olefines. With conjugated dienes considerable evolution of HBr takes place; this reaction is sp. for such dienes, and can serve for their identification in mixtures with other hydrocarbons. R. T.

Determination of ammonia and carbamide by modification of the Conway diffusion method.—See A., 1941, I, 426.

Gasometric determination of amino-acids.—See A., 1941, III, 947.

Micro-chemical reaction for detection of celandine.—See A., 1941, III, 819.

BRITISH CHEMICAL AND PHYSIOLOGICAL ABSTRACTS

A., II.—Organic Chemistry

DECEMBER, 1941.

I.—ALIPHATIC.

Dehydrogenation of *n*-heptane and *cyclo*hexane on cerium, vanadium, and thorium catalysts.—See A., 1941, I, 478.

Thermal decomposition of ethylidene bromide.—See A., 1941, I, 473.

Reaction of olefines with solid cuprous halides. E. R. Gilliland, H. L. Bliss, and C. E. Kip (*J. Amer. Chem. Soc.*, 1941, **63**, 2088—2090).—C_2H_2 and butadiene with solid CuCl give compounds X,2CuCl (X = olefine). Isoprene yields a compound of the approx. formula C_5H_8,3CuCl but this may be due to incomplete reaction. Amylene and *cyclo*pentadiene do not give detectable compounds with CuCl. W. R. A.

Polymerisation of olefines. V. Isomerides [contained] in tri*iso*butylene. F. C. Whitmore, C. D. Wilson, J. V. Capinjola, C. O. Tongberg, G. H. Fleming, R. V. McGrew, and J. N. Cosby. **VI. Dimerides obtained from tetramethylethylene.** F. C. Whitmore and P. L. Meunier. **VII. Isolation and oxidation of αα-dineopentylethylene.** F. C. Whitmore and J. D. Surmatis (*J. Amer. Chem. Soc.*, 1941, **63**, 2035—2041, 2197—2199, 2200—2201; cf. A., 1941, II, 237).—V. Efficient fractionation (75, later 90—100, theoretical plates) of tri*iso*butylene gives fractions, (*A*) (75%), b.p. 177·7°, (*B*) (15%), b.p. 179·0°, and (*C*) (10%), b.p. 183—185°, unchanged by further fractionation, extraction with NH_2Ph or MeOH, or equilibrium melting. (*A*) is a mixture of $CH_2{:}C(CH_2Bu^{\gamma})_2$ (**I**) and the lower-boiling isomeride of $CHBu^{\gamma}{:}CMe{\cdot}CH_2Bu^{\gamma}$ (**II**), since ozonolysis in AcOH (less well, saturated hydrocarbons, b.p. 0—30°, and not other solvents) gives $Bu^{\gamma}CHO$, $COMe{\cdot}CH_2Bu^{\gamma}$ (**III**), CH_2O, $CO(CH_2Bu^{\gamma})_2$ (**IV**), m.p. −10°, b.p. 63°/11 mm. (*oxime*, m.p. 78°), and $Bu^{\gamma}CO_2H$. (*B*) is similarly shown to contain mainly the higher-boiling isomeride of (**II**) and less (**I**). By ozonolysis of (*A*) and (*B*) $(CH_2Bu^{\gamma})_2CH{\cdot}CO_2H$ and $CH_2Bu^{\gamma}{\cdot}CMeBu^{\gamma}{\cdot}CO_2H$, both known to be derived from (**I**) and (**II**), are also obtained. (*C*) contains $CH_2{:}CMe{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2Bu^{\gamma}$ and $CMe_2{:}CH{\cdot}CMe_2{\cdot}CH_2Bu^{\gamma}$, since ozonolysis yields CH_2O, *ααγγ-tetramethyl*-n-*valeric acid* (**V**), m.p. 40—45°, b.p. 123°/15 mm. (*amide*, m.p. 70—71°; *β-keto*-n-*propyl* ester *semicarbazone*, m.p. 155°), *δδζζ-tetramethyl*-n-*heptan-β-one* (**VI**), b.p. 75°/10 mm. (*semicarbazone*, m.p. 149°), and usually $Bu^{\gamma}CO_2H$, (**IV**), and (by a side-reaction) $CH_2Bu^{\gamma}{\cdot}CMe_2{\cdot}OH$ (**VII**), b.p. 143—145°. The structure of (**VII**) is proved by dehydration by 20% H_2SO_4 to di*iso*butylene, identified by oxidation (CrO_3). That of (**V**) is proved by Curtius degradation to $CH_2Bu^{\gamma}{\cdot}CMe_2{\cdot}NH_2$ (*phenylcarbamide* derivative, m.p. 137°; *Ac* derivative, m.p. 98—99°), also prepared from $CH_2Bu^{\gamma}{\cdot}CMe_2Cl$ by AgCNO, followed by KOH. Oxidation of (**VI**) by CrO_3 in dil. H_2SO_4 gives ~21% of (**V**) and 20% of AcOH. (**VI**) gives no CHI_3, but with MgPhBr gives an alcohol, b.p. 139°/5 mm., converted by dehydration into (**I**) and then ozonolysis into COPhMe and CH_2O. Ozonolysis of (**II**) is more rapid than that of (**I**). (**IV**) is synthesised in 60% yield from $CH_2Bu^{\gamma}{\cdot}MgCl$ and $CH_2Bu^{\gamma}{\cdot}COCl$ in Et_2O. Polymerisation of $CH_2{:}CMe_2$ by H_2SO_4 proceeds by reversible formation of $Bu^{\gamma}HSO_4$, the electronically deficient so-called carbonium "ion" $Bu^{\gamma+}$ and HSO_4^-, and related more complex products; its exact course is in doubt.

VI. The dimeride, b.p. 70—100°/100 mm., obtained in 62% yield from $(CMe_2{:})_2$ by 80% H_2SO_4 at 0°, contains $CHMePr^{\beta}{\cdot}CH{:}CMeBu^{\gamma}$ (50), $CMe_2{:}CMe{\cdot}CHMe{\cdot}CH_2Bu^{\gamma}$ (10) (cf. Brunner *et al.*, A., 1937, II, 395), $CHBu^{\gamma}{:}CMe{\cdot}CH_2Bu^{\gamma}$ (25), and $CH_2{:}C(CH_2Bu^{\gamma})_2$ (0·2%), since fractionation and then ozonisation in saturated light petroleum yields pinacolone, $CHMePr^{\beta}{\cdot}CHO$, $COMe_2$, (**III**), $Bu^{\gamma}CHO$, $COMe{\cdot}CHMe{\cdot}CH_2Bu^{\gamma}$, CH_2O, and (**IV**). The mechanism of the reaction, discussed in detail and shown to differ fundamentally from that of polymerisation by BF_3, combines rearrangement and polymerisation.

VII. Oxidation of tri*iso*butylene by $Na_2Cr_2O_7$ in aq. H_2SO_4 at 50—60° gives 18% of unattacked, pure $CH_2{:}C(CH_2Bu^{\gamma})_2$ (**VIII**), b.p. 112—113°/100 mm., which on further oxidation at 50—60° and later 80° gives $(CH_2Bu^{\gamma})_2CH{\cdot}CO_2H$ (24·7), m.p. 93—94°, unchanged (**VIII**) (46), (**IV**), (1·9), ketones (~9%) of higher b.p., and smaller amounts of (**III**), $Bu^{\gamma}CO_2H$, and $CH_2Bu^{\gamma}{\cdot}CO_2H$. R. S. C.

Mechanism of photochemical change of acetylene.—See A., 1941, I, 480.

Polymerisation of hydrocarbons of the C_nH_{2n-4} series with vicinal double and triple linkings. II. Cyclic dimerisation of *iso*propenylacetylene. A. I. Zacharova and V. A. Bezel-Sitscheva (*J. Gen. Chem. Russ.*, 1941, **11**, 67—69).—. $CH_2{:}CMe{\cdot}C{:}CH$ in MeOH is converted by heating for 12 hr. at 120° into *m-iso*propenyltoluene. R. T.

High-temperature chlorination of saturated, aliphatic monochlorides. Vicinal effect. F. F. Rust and W. E. Vaughan (*J. Org. Chem.*, 1941, **6**, 479—487).—Investigation of the vapour-phase chlorination of EtCl, $Pr^{\alpha}Cl$, $Pr^{\beta}Cl$, $Bu^{\alpha}Cl$, and $Bu^{\beta}Cl$ shows that the C·Cl group in a straight-chain aliphatic monochloride markedly retards substitution on the adjacent (once-removed) C atoms, the effect becoming increasingly pronounced with progressively higher temp. This "vicinal" effect extends in a smaller degree to the C twice removed from the C·Cl group. In this type of chlorination substitution of H on C linked to Cl is mildly retarded, the effect decreasing with increasing temp. Thus the small amount of $CH_2Cl{\cdot}CHEtCl$ formed from $Bu^{\alpha}Cl$ at 202° decreases when the chlorination is performed at a higher temp. At the same time, the relative reactivity of the H atoms of CH_2Cl steadily increases in comparison with those of the uninfluenced Me; the reactive *sec.* H at $C_{(\gamma)}$ are seemingly not greatly affected. In the chlorination of $Pr^{\alpha}Cl$ a progressive decrease in the proportion of $CHMeCl{\cdot}CH_2Cl$ is observed with rise of temp. while the relative reactivities of the H at $C_{(\alpha)}$ and $C_{(\gamma)}$ are enhanced. Examination of the chlorination of EtCl, $Pr^{\alpha}Cl$, and $Bu^{\alpha}Cl$ at 310—320° shows that the "vicinal" effect of Cl in the monochloride is not confined to the C·H linking on the once-removed C atoms but extends at least to those twice removed. Substitution into Me of $Pr^{\alpha}Cl$ does not occur as readily as it does into CH_2Cl. Only when Me is sufficiently removed from Cl, as in $Bu^{\alpha}Cl$, do its H atoms approach the reactivity of those in C_2H_6. H. W.

Reaction of halogens and iron with alcohols and esters. IV. Reaction of iron and bromine with ethyl alcohol. M. T. Dangjan (*J. Gen. Chem. Russ.*, 1941, **11**, 108).—EtBr is obtained in 81% yield when Br is added to a suspension of Fe in EtOH. R. T.

Allylic rearrangements. XI. Action of magnesium and zinc on crotyl and methylvinylcarbinyl chlorides. W. G. Young and M. Eisner (*J. Amer. Chem. Soc.*, 1941, **63**, 2113—2115; cf. A., 1940, II, 148).—86% of $C_4H_7{\cdot}MgCl$ is obtained from 30 : 15 : 1 Et_2O–Mg–C_4H_7Cl. The butenes obtained from mixtures of $CHMe{:}CH{\cdot}CH_2Cl$ (**I**) and $CH_2{:}CH{\cdot}CHMeCl$ by Mg–Et_2O or activated Zn in boiling 80% EtOH are independent of the nature of the mixture [8—93·5% of (**I**)], but depend on the metal + solvent; *e.g.*, Mg gives ~54·5% of Δ^{α}-, ~20·5% of *cis*-Δ^{β}-, and ~25% of *trans*-Δ^{β}-C_4H_8, and Zn–EtOH gives 67·4, 32·6, and <2%, respectively. With Mg, C_4H_7Br gives the same butenes (56·4±2·0,

17·2±3·3, and 25·5±1·4%, respectively), but with Zn–EtOH gives a different mixture (62, 30, and 7, all ±2—3%, respectively). Use of abs. EtOH or $Pr^{\beta}OH$ instead of 80% EtOH with Zn and C_4H_7Br has no effect on the ratio of products. R. S. C.

Preparation of tetradeuteroethylene dibromide by direct union of dideuteroacetylene and deuterium bromide. Route to tetradeuteroethylene. C. L. Wilson and A. W. Wylie (*J.C.S.*, 1941, 596—601).—C_2H_2 and HBr, thoroughly mixed, and a C catalyst (granular charcoal activated in HBr at 450°) at ~200° give 70% yields of $(CH_2Br)_2$, with some $CHMeBr_2$, $CH_2{:}CHBr$ (**I**), and EtBr; the walls of the glass reaction tube probably catalyse union between (**I**) and HBr; higher temp. gives increased yields of (**I**). When a change to D compounds is made, it is necessary first to replace the exchangeable H in the catalyst by D, which is carried out by prolonging the activation process using DBr at 450°. An all-glass apparatus for producing a continuous supply of DBr by combination of electrolytic D and Br is described. DBr and C_2D_2 at 180° give products of similar composition to that obtained with "light" materials, and yield isomeric dibromotetradeuteroethanes (D content = ~99 at.-%), with a little $CD_2{:}CDBr$ and C_2D_5Br. C_2D_4 is prepared from the mixed isomerides by reaction with Zn in moist dioxan (+D_2O) and combination with Br affords the pure dibromide. A. T. P.

Promoting action of mercury on aluminium oxide in the dehydration of ethyl alcohol.—See A., 1941, I, 478.

Vapour-phase catalytic conversion of methyl*tert.*-butylcarbinol. E. A. Kelso, G. Wash, J. T. Horeczy, B. Shive, and W. A. Felsing (*J. Amer. Chem. Soc.*, 1941, **63**, 2273—2274).—In presence of commercial Al_2O_3 at 293—305°, $CHMeBu^{\gamma}{\cdot}OH$ gives $(CMe_2{:})_2$ 52, $CH_2{:}CMePr^{\beta}$ 32, and $CH_2{:}CHBu^{\gamma}$ 16%. The proportion of isomerides thus depends on the activity of the Al_2O_3 (cf. Brooks *et al.*, A., 1940, I, 201; Cramer *et al.*, A., 1939, II, 136). R. S. C.

Dehydration of *tert.* carbinols containing the neopentyl group. F. C. Whitmore and E. Rohrmann (*J. Amer. Chem. Soc.*, 1941, **63**, 2033—2035).—When $CH_2Bu^{\gamma}{\cdot}CR_2{\cdot}OH$ is dehydrated by anhyd. $CuSO_4$ and pumice, the CH_2Bu^{γ} is barely affected. The structure of the products below is proved by ozonolysis.
$CH_2Bu^{\gamma}{\cdot}CEt_2{\cdot}OH$ (prep. from $Bu^{\gamma}{\cdot}[CH_2]_2{\cdot}CO_2Et$ and MgEtBr), b.p. 32°/3 mm., at 180—190° gives ~9 parts of $CHMe{:}CEt{\cdot}CH_2Bu^{\gamma}$ and 1 part of $CEt_2{:}CHBu^{\gamma}$.
$CH_2Bu^{\gamma}{\cdot}CMeBu^{\alpha}{\cdot}OH$ (prep. from $COMe{\cdot}CH_2Bu^{\gamma}$ and $MgBu^{\alpha}Br$), b.p. 55—56°/5 mm., at 193—198° gives >8 parts of $CHPr^{\alpha}{:}CMe{\cdot}CH_2Bu^{\gamma}$, 1 part of $CH_2{:}CBu^{\alpha}{\cdot}CH_2Bu^{\gamma}$, and a trace of $CHBu^{\gamma}{:}CMeBu^{\alpha}$. R. S. C.

***cis*- and *trans*-Forms of βε-dimethyl-Δ$^{\gamma}$-*n*-hexene-βε-diol.** (A) J. Salkind. (B) J. R. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 2282).—(A) Bourguel's substance, m.p. 101°, was shown (Salkind *et al.*, A., 1938, II, 123) to be a form of $(CH{\cdot}CMe_2{\cdot}OH)_2$ (cf. Johnson *et al.*, A., 1941, II, 1).

(B) This correction is confirmed by hydrogenation of the substance by $2H_2$–PtO_2 to $(CH_2{\cdot}CMe_2{\cdot}OH)_2$, m.p. 88·5°, and by $1H_2$–Pd to $(CH{\cdot}CMe_2{\cdot}OH)$, m.p. 68—69°. The structure, *trans*-$(CH{\cdot}CMe_2{\cdot}OH)_2$, for Salkind's substance, m.p. 75°, requires confirmation. R. S. C.

Aliphatic sulphonic acids. Synthesis and properties of acylamides of aliphatic sulphonic acids. A. G. Kostzova (*J. Gen. Chem. Russ.*, 1941, **11**, 63—66).—The following have been prepared by standard methods: *chloromethanesulphonyl chloride*, b.p. 60°/10 mm., *chloromethanesulphon-acetamide*, m.p. 146°, and *-benzamide* (**I**), m.p. 118°, *α-chloroethanesulphonacetamide*, m.p. 114°, and *-benzamide* (**II**), m.p. 123°, *benzylsulphon-acetamide*, m.p. 129°, and *-benzamide*, m.p. 148°. (**I**) and (**II**) are intensely sweet. R. T.

Reactions of carboxylic esters. M. P. Balfe and J. Kenyon (*Nature*, 1941, **148**, 196).—Although acid- or alkali-catalysed hydrolysis or esterification, and alkoxy-interchange, take place usually by mechanisms in which the linkings of the alkoxyl C are not disturbed, the alternative mechanism involving rupture between O and Alk occurs, to a greater extent than has been recognised, when the OAlk has electron-releasing properties. Reactions which can be explained on the assumption that the esters dissociate according to the second manner are quoted. L. S. T.

Acylals. C. D. Hurd and F. O. Green (*J. Amer. Chem. Soc.*, 1941, **63**, 2201—2204).—Compounds, $CHR(O{\cdot}COR')_2$ and $OR''{\cdot}CHR{\cdot}O{\cdot}COR'$ (*A*) (R, R', and R'' = alkyl or aryl), are termed acylals. Acylals, exemplified by $CHMe(OAc)_2$, react with NH_2Ph, thus: → NHPhAc + [OH·CHMe·OAc] → MeCHO + AcOH; with $3NH_2OH$, thus: → NHAc·OH + $CHMe{:}N{\cdot}OH$ + $OH{\cdot}NH_2{\cdot}OAc$ + H_2O (method of analysis detailed); and with Cl_2 at 90—100° (no reaction at room temp.) to give $CCl_3{\cdot}CHO$, $CHCl_2{\cdot}CHO$, AcOH, and $CH_2Cl{\cdot}CO_2H$ with some $CH_2Cl{\cdot}CH(OAc)_2$ and $CHCl_2{\cdot}CH(OAc)_2$. RCHO, HCl, and R'OH give ~80% of $CHRCl{\cdot}OR'$, which with $R''CO_2Na$, first at 0° and then warm, gives 40—74% of (*A*) and a higher-boiling residue. Thus are obtained: *α-methoxyethyl acetate*, b.p. 24—25°/15 mm., *propionate*, b.p. 41—43°/18 mm., and *butyrate*, b.p. 44—45°/11 mm.; *α-ethoxyethyl propionate*, b.p. 51—51·5°/18 mm., and *butyrate*, b.p. 55—56°/11 mm.; *α-propoxyethyl acetate*, b.p. 54—55°/20 mm., *propionate*, b.p. 54·8—55·2°/11 mm., and *butyrate*, b.p. 67·8—69°/11 mm.; *α-butoxyethyl acetate*, b.p. 69·5—70°/21 mm., *propionate*, b.p. 70—71°/11 mm., and *butyrate*, b.p. 80—81°/11 mm.; *α-ethoxypropyl acetate*, b.p. 46·3—46·8°/14 mm.; *α-ethoxybutyl acetate*, b.p. 53—54°/10 mm., and *propionate*, b.p. 66—67°/10 mm. *n* and *d* are recorded. R. S. C.

Tracer studies using radioactive carbon. Oxidation of propionic acid. P. Nahinsky and S. Ruben (*J. Amer. Chem. Soc.*, 1941, **63**, 2275—2276).—Using radioactive C*, it is shown that EtC^*O_2H, prepared from MgEtBr and C^*O_2, with $KMnO_4$ gives C* in both $H_2C_2O_4$ and CO_2 but with $K_2Cr_2O_7$ gives only AcOH and C^*O_2, both oxidations being quant. R. S. C.

Reliability of reactions used to locate assimilated carbon in propionic acid. H. G. Wood, C. H. Werkman, A. Hemingway, A. O. Nier, and C. G. Stuckwisch (*J. Amer. Chem. Soc.*, 1941, **63**, 2140—2142).—When $Et^{13}CO_2H$, prepared from MgEtBr and $^{13}CO_2$ (4·92% of the CO_2 used), is oxidised by $KMnO_4$–NaOH, the ^{13}C is obtained partly in the $Na_2C_2O_4$ and partly in the Na_2CO_3. At 460° reaction occurs strictly according to $(Et^{13}CO_2)_2Ba$ → $^{13}COEt_2$ + $Ba^{13}CO_3$. R. S. C.

Migration of acyl groups during hydrogenation of triglycerides. D. Atherton and T. P. Hilditch (*J.C.S.*, 1941, 527—535; cf. B., 1938, 79).—During the hydrogenation of mixtures of glycerides at 180° in presence of Ni on kieselguhr, interchange of acyl groups between the mols. of the triglycerides is slow; ~5% of the total glycerides are involved per hr. of exposure to hydrogenation conditions. Interchange of acyl groups proceeds between completely saturated glycerides, *i.e.*, is not dependent on concurrent hydrogenation. The change appears to occur more readily between simple triglycerides than when one component is a mixed triglyceride, *e.g.*, oleodipalmitin or palmitodiolein (**I**). Appreciable interchange occurs between tripalmitin (**II**) and triolein (**III**) or tristearin (**IV**), but is much less evident in mixtures of oleo- or stearo-dipalmitin and (**III**) or (**IV**), and occurs only slightly during hydrogenation of mixtures of (**I**) and (**III**). Conclusions from analytical data in these cases, however, are only of qual. significance. The presence of unresolved ternary mixtures in the final crystal fractions is less likely to occur in the case of hydrogenation of a mixture of (**III**) and (**V**), and this allows a more reliable estimation of (**IV**) and (**V**). After 3 hr. 20 min., ~14% of the glycerides undergo acyl interchange, and after 12·5 hr., 37% of interesterification is noted. The mixed triglycerides produced in both cases are probably almost wholly dilaurostearin, and laurodistearin is formed in small amounts only. When hydrogenation of a mixture of (**III**) and (**II**) is interrupted before completion (105 min.; I val. of 18·3), or when a similar mixture is heated at 180° in presence of catalytic Ni in CO_2 for 9 hr., the product contains a small proportion of mixed glycerides containing both palmitic and oleic acids. Results are considered in relation to the procedure adopted for determining the proportion of tri-C_{18} glycerides in fats by hydrogenation, followed by estimation of (**IV**) in the products; when this procedure is essential, hydrogenation should be rapid at 65—70° using Raney Ni, Pd, or Pt catalysts. The possible effect of time of hydrogenation, involving variations in degree of acyl interchange, on the texture and other properties of technically hydrogenated fats is indicated. A. T. P.

Polymerisation and drying of oils and esters of fatty acids. I. Theory of polymerisation. A. J. Drinberg. **II. Heat of polymerisation and nature of polymerides of oils.** A. J. Drinberg and A. I. Schepelev. **III. Heat of drying of linseed oil.** A. J. Drinberg and V. G. Juschin (*J. Gen. Chem.*

Russ., 1940, **10**, 2052—2058, 2059—2064, 2065—2072).—I. Polymerisation of drying oils involves reactions between C:C groups and of carbalkoxy-groups. Possible modes of polymerisation are reviewed, and methods of calculating polymerisation coeffs. are discussed.

II. The heat of polymerisation, Q, of oils is determined as the difference between the heat of combustion of the oil and of the polymeride. Derived formulæ for calculating Q give results in satisfactory agreement with experimental vals. for linseed (I), sunflower seed (II), and cottonseed oils (III) polymerised at 300° in an atm. of N_2. The results indicate that the ratio of intra- to inter-mol. reaction of reactive groups is 2 : 1 in the case of (I) and (II) oil, and 3 : 2 in that of (III).

III. The velocity and the heat of drying of (I) rise with increasing temp. from 20° to 98°. At 20° the reaction is of an auto-oxidative type, but with rising temp. direct oxidation becomes increasingly important. R. T.

Photolysis of some chloronitroso-compounds. S. Mitchell, K. Schwarzwald, and G. K. Simpson (*J.C.S.*, 1941, 602—605; cf. A., 1939, I, 89).—*γ-Chloro-γ-nitrosovaleric acid* (I) and *β-chloro-β-nitroso-αδ-diphenylbutane* (II) have been prepared by the action of Cl_2 on the oximes of lævulic acid and of αδ-diphenylbutan-β-one, respectively. Both (I) and (II) form blue crystals, m.p. 33° and 46°, respectively. (I) decomposes slightly when kept. The absorption spectra of (I) and (II) in MeOH solution are recorded from 7460 to 6590 A. The quantum efficiencies, γ, of the decomp. in MeOH solution of (I) and (II) and of 1-chloro-1-nitroso*cyclo*hexane (III) and β-chloro-β-nitroso-γγ-dimethylbutane (IV) have been measured at the λ of max. absorption in each case. γ for (I) and (II) is ~1 at this λ, whilst for (II) and (IV) vals. are 0·78 and 0·62, respectively. At shorter λ, γ for (II) and (IV) becomes ~1. The products of decomp. in all cases contain 90—100% of the theoretical HCl. Other products are: for (I), the oxime hydrochloride of Me lævulate, $C_6H_{12}O_3NCl$, and a small amount of Me lævulate; for (II) the oxime of αδ-diphenylbutan-β-one and CH_2O. O. D. S.

Acyloins. IX. Non-enzymic decarboxylation of pyruvic acid and acetoin formation. W. Dirscherl and H. Nahm (*Z. physiol. Chem.*, 1940, **264**, 41—56; cf. A., 1931, 1457).—$AcCO_2H$ is decarboxylated by various NH_2-acids [*e.g.*, *l*(−)-tyrosine (I), *dl*-alanine, *dl*-serine, *l*(−)-proline, and *l*(+)-arginine at 100°; *dl*-tyrosine at 120° (not at 54°); reaction generally accelerated in presence of C_5H_5N], aneurin (II) at 120° (not particularly active), or quinine at 100° (unaffected by C_5H_5N). Formation of acetoin (III) thereby occurs with, *e.g.*, *dl*- or *l*(+)-alanine, *dl*- or *l*(−)-asparagine or -aspartic acid, and *dl*-NH_2·CHPh·CO_2H, but not with, *e.g.*, (I), (II), *dl*-cystine, or *dl*-leucine. Use of (−)-NH_2·CHPh·CO_2H or *l*(−)-asparagine leads to optically inactive (III), whereas a mixture of (−)- and *dl*-(III) is formed during decarboxylation by yeast carboxylase (cf. A., 1938, III, 442). The significance of these results in connexion with the "carboligase" question is discussed. *l*(+)-Alanine, *l*(−)-aspartic acid, and (+)-NH_2·CHPh·CO_2H are more or less rapidly racemised by hot AcOH or $AcCO_2H$; *l*(−)-leucine is more stable. H. B.

Hydrogenation of acetylenic compounds. XXXIII. Synthesis and catalytic hydrogenation of acetylenic hydroxy-acids. J. S. Salkind and B. I. Michantiev (*J. Gen. Chem. Russ.*, 1941, **11**, 92—98).—A solution of (:C·MgBr)$_2$ when saturated with CO_2–$COMe_2$ mixture yields *γ-hydroxy-γ-methyl-*Δ^{α}*-pentinene-α-carboxylic acid*, an oil (*amide*, m.p. 72—73°), converted by hydrogenation (Pd and Pt) into *γ-iso*hexolactone. When $COPh_2$ replaces $COMe_2$ in the above reaction the product is *γ-hydroxy-γγ-diphenyl-*Δ^{α}*-butinene-α-carboxylic acid*, m.p. 78—80° (*amide*, m.p. 96—97°), hydrogenated to OH·CPh_2·$[CH_2]_2$·CO_2H. R. T.

Alkyl carbonates in synthetic chemistry. II. Condensation with ketones. Synthesis of β-keto-esters. V. H. Wallingford, A. H. Homeyer, and D. M. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 2252—2254; cf. following abstract).—The reaction, COMeR + Et_2CO_3 (or Me_2CO_3) + NaOEt → COR·CHNa·CO_2Et + 2EtOH, is realised in yields up to 74% by heating COMeR in an excess of Et_2CO_3 with NaOEt, NaOEt–EtOH, or NaOMe with continuous removal of EtOH. The method is limited by (*a*) self-condensation of very reactive ketones and (*b*) formation of ethers and $NaEtCO_3$ at >100° when reaction is "forced" for non-reactive ketones. *O*-Carboxylation and subsequent decarbomethoxylation may occur; thus COPhEt, COPhPr, and *cyclo*hexanone give 25%, 15%, and only (20%) esters of type CO_2Et·O·CPh:CR. In examples R = Pr$^{\beta}$, Bu$^{\gamma}$, Bu$^{\beta}$, *n*-amyl, CH_2Bu^{γ}, Ph, *p*-C_6H_4Me, -C_6H_4Cl, -C_6H_4·OMe, and -C_6H_4·OEt; $COEt_2$, $COPr^{\alpha}_2$, COPhEt, COPhPr, COPh·CH_2Ph, $CO(CH_2Ph)_2$, and *cyclo*hexanone are also used. The following are incidentally described. *Et β-keto-*δδ*-dimethyl*-n-*hexoate*, b.p. 104—105°/15 mm.; *Et* p-*ethoxybenzoylacetate*, m.p. 53—54°; 1-*phenyl*-3-iso*propyl*-, m.p. 81—83°, *-neopentyl*-, m.p. 138—140°, and *-p*-chlorophenyl-5-pyrazolone, m.p. 161° (lit. 140°); 3-p-*ethoxyphenyl*-5-iso*oxazolone*, m.p. 135—136°. When KOPr–PrOH is used, *n*-C_6H_{13}·COMe gives *Pr$^{\alpha}$ β-keto*-n-*nonoate*, b.p. 104—105°/15 mm. When KOBu–BuOH is used, COPhMe gives *Bu$^{\alpha}$ benzoylacetate*, b.p. 120—125°/1 mm. R. S. C.

Alkyl carbonates in synthetic chemistry. I. Condensation with organic esters. Synthesis of malonic esters. V. H. Wallingford, A. H. Homeyer, and D. M. Jones (*J. Amer. Chem. Soc.*, 1941, **63**, 2056—2059).—The reaction, $CH_2R'·CO_2R$ + R_2CO_3 + NaOR (or NaOR–ROH) ⇌ $CR'Na(CO_2R)_2$ + 2ROH, is forced to the right by heating under reflux in an excess of R_2CO_3 with continuous removal of the alcohol formed and then becomes preparative for $CHR'(CO_2R)_2$. The method is particularly good if R′ = aryl, but succeeds in the purely aliphatic series up to Et and Bu stearate and Et oleate. In examples, R = Et, Pr, or Bu. In the aliphatic series *C*-alkylation by R_2CO_3 may also occur; thus, $Pr^{\alpha}CO_2Et$ gives $CHEt(CO_2Et)_2$ 45 and $CEt_2(CO_2Et)_2$ 10, *n*-C_5H_{11}·CO_2Et gives $CHBu^{\alpha}(CO_2Et)_2$ 26 and $CEtBu^{\alpha}(CO_2Et)_2$ 34, $Bu^{\beta}CO_2Et$ gives $CHPr^{\beta}(CO_2Et)_2$ 30 and $CEtPr^{\beta}(CO_2Et)_2$ 10, and *iso*-C_5H_{11}·CO_2Et gives *iso*-C_5H_{11}·CO_2Et 30 and *iso*-C_5H_{11}·$CEt(CO_2Et)_2$ 45%. Acylation or alkylation of the $CR'Na(CO_2Et)_2$ produced can be effected without isolation of the $CHR'(CO_2Et)_2$. $CHR'R''·CH_2·CO_2Et$ reacts, but not $CR'_3·CO_2Et$ (*e.g.*, $Bu^{\gamma}CO_2Et$) or $CHR'R''·CO_2Et$ ($CHPhEt·CO_2Et$, $CHEt_2·CO_2Et$). EtOAc gives $CH_2(CO_2Et)_2$ 25 and $CH(CO_2Et)_3$ 10, $CH_2(CO_2Et)_2$ gives $CH(CO_2Et)_3$ 10, and Et_2 sebacate gives $CO_2Et·[CH_2]_7·CH(CO_2Et)_2$ (b.p. 185—198°/1·5 mm.) 60%. n-*Decylmalonic acid*, m.p. 118—119·5°, *Et$_2$* p-*iodo*-, b.p. 165°/1·5 mm., and 3 : 4-*dimethoxy-phenylmalonate*, b.p. 170°/1 mm., are incidentally described. R. S. C.

Grignard synthesis of glucosaccharic acid from *l*-arabinose. A. M. Gachokidze (*J. Gen. Chem. Russ.*, 1941, **11**, 109—116).—*l*-Arabinosazone and HCl yield l-*arabosone*, a syrup, oxidised by aq. Br to *α-keto*-l-*arabonic acid*, a syrup, $[\alpha]_D$ −61·2° in H_2O (*Ca* and *Ba* salts; *phenylhydrazide-phenylhydrazone*, m.p. 131°; Ac_2 derivative, m.p. 165°), which with Me_2SO_4 affords *Me α-keto-*γδε*-trimethylarabonate*, a syrup, $[\alpha]_D$ −59·8° in $CHCl_3$. With MgMeI in Et_2O–$CHCl_3$ this gives *Me* γδε*-trimethylsaccharate*, a syrup, $[\alpha]_D$ −10·5° in $CHCl_3$, hydrolysed by 8% H_2SO_4 to the *acid*, a syrup, $[\alpha]_D$ −21·4° (*Ca* and *Ba* salts), reduced by HI to *δ-hydroxypentane-β-carboxylic acid*, m.p. 139° (*Ba* salt). R. T.

Identification of carbonyl compounds by the use of 3-carbohydrazido-1-methylpyridinium *p*-toluenesulphonate. C. F. H. Allen and J. W. Gates, jun. (*J. Org. Chem.*, 1941, **6**, 596—601).—*3-Carbohydrazido-1-methylpyridinium* p-*toluenesulphonate* (I), m.p. 160° (metastable variety, m.p. 130—131°), is obtained by the successive action of *p*-$C_6H_4Me·SO_3Me$ and N_2H_4,H_2O on Et nicotinate in boiling EtOH. It reacts with many CO compounds (II) in boiling EtOH, giving well-cryst. products which are usually crystallised from boiling EtOH and from which (II) are smoothly regenerated by warm dil. acids. They may be readily converted into other derivatives of (II); *e.g.*, the 2 : 4-dinitrophenylhydrazone may be made by warming the compound with dil. mineral acid and adding 2 : 4 : 1-$(NO_2)_2C_6H_3·NH·NH_2$ directly to the resulting solution. The *-hydrazones* of the following -aldehydes have been characterised: *acet*-, m.p. 187°; *prop*-, m.p. 171°; n-*but*-, m.p. 168°; iso*but*-, m.p. 173°; n-, m.p. 142°, and iso-, m.p. 159°, *-valer*-; n-*hex*-, m.p. 153°; n-*hept*-, m.p. 160°; n-*oct*-, m.p. 154°; n-*non*-, m.p. 152°; n-*dec*-, m.p. 152°; n-*undec*-, m.p. 142°; n-*dodec*-, m.p. 145°; n-*tetradec*-, m.p. 142°; *α-methyl*-n-*non*-m.p. 132°; *α-ethyl*-n-*but*-, m.p. 137°; *α-ethyl*-n-*hex*-, m.p. 131°; *croton*-, m.p. 193°; *α-methyl-β-ethylacr*-, m.p. 182°; *α-ethyl-β*-n-*propylacr*-, m.p. 197°; *citronellal*, m.p. 142°; n-Δ^{ω}-*undecylen*-, m.p. 145°; *furfur*-, m.p. 164°; *benz*-, m.p. 211°; *cumin*-, m.p. 259°; *phenylacet*-, m.p. 165°; *hydralrop*-, m.p. 125°; *β-phenylprop*-, m.p. 160°; *cinnam*-, m.p. 235°; p-iso*propylcinnam*-, m.p. 241°; *α*-n-*propylcinnam*-, m.p. 187°; *α*-n-*butylcinnam*-, m.p. 163°; *α*-n-*amylcinnam*-, m.p. 126°;

α-n-*hexylcinnam-*, m.p. 113°. The *-hydrazones* of the following ketones are described: cyclo*pentanone*, m.p. 181°; cyclo*hexanone*, m.p. 146°; cyclo*pentadecanone*, m.p. 144°; 2-*heptyl*cyclo*pentanone*, m.p. 136°; iso*phorone*, m.p. 156°; *COMe*$_2$, m.p. 166°; *Me octyl*, m.p. 109°, *Me nonyl*, m.p. 110°, and *Me decyl*, m.p. 111°, *ketone*; *β-ionone*, m.p. 147°; *Ac*$_2$, m.p. 264°; *CH*$_2$*Ac*$_2$, m.p. 212°; *COPhMe*, m.p. 191°; p-sec.-*amylacetophenone*, m.p. 143°; *CH*$_2$*BzCl*, m.p. 120°; 2:4-*dimethylphenacyl chloride*, m.p. 196°; *COMe·CH*$_2$*Cl*, m.p. 135°; *COMe·CHCl*$_2$, m.p. 115°; *CH*$_2$*Cl·COEt*, m.p. 137°; *CH*$_2$*Ac·CH*$_2$*·CO*$_2$*Et*, m.p. 136°; *CH*$_2$*Ac·CH*$_2$*·CO*$_2$*Me*, m.p. 160°; *β-chloropropiophenone*, m.p. 171°. (I) does not react or gives non-cryst. products with the following: CH_2O, CH_2BzBr, α-ionone, technical ionone, Me and Ph vinyl ketone, heptylideneacetone, 2-heptylidene*cyclo*pentadecanone, mesityl oxide, diacetone alcohol, hydroxycitronellal, glucose, COMe·CH:CHPh, $CH_2Ac·CH_2·CO_2H$, phorone, fenchone, $COBu^{\alpha}_2$, $COBu^{\beta}_2$, chloral, and 2:5-dimethylfuran. M.p. arc corr. H. W.

Catalysis of aldol condensation of acetaldehyde by amino-acids. E. V. Budnitzkaja (*Biochimia*, 1941, **6**, 146—154).—At 35—37° and neutral reaction, NH_2-acids catalyse the conversion of MeCHO into aldol (I), glycine being more active than alanine, which is more active than aspartic acid. The rate of conversion increases with increase in p_H and NH_2-acid concn. Products of higher mol. wt. than (I) are also produced. Org. N compounds other than NH_2-acids (*e.g.*, amines, amides, and to a small extent peptones, diketopiperazine, and ovalbumin) also catalyse the conversion. The action depends on the enolisation of MeCHO by the catalysts. NH_2-acids or analogous substances possibly catalyse the synthesis of C chains in the living cell. W. McC.

Semicarbazone of the methyl ester of azelaic half-aldehyde. F. Bergmann (*J. Amer. Chem. Soc.*, 1941, **63**, 2279).—$CO_2Me·[CH_2]_7·CHO$, b.p. 159—164°/26 mm. (*semicarbazone*, m.p. 107°), is obtained from Me θ_i-dihydroxystearate by $Pb(OAc)_4$. R. S. C.

Effect of structure on reactivity of carbonyl compounds; temperature coefficients of rate of formation of semicarbazones.—See A., 1941, I, 474.

Catalytic hydrogenation of organic compounds. I. Hydrogenation of acetone. K. Akashi (*Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 422—430).—The composition of Ni catalysts exercises a marked influence on the reaction products. The following substances are obtained by hydrogenating $COMe_2$ with the catalysts and at the temp. indicated: Ni (110°) $Pr^{\beta}OH$, (300°) CH_4; Ni + B_2O_3 (210°) C_3H_8, (290°) C_3H_8, CH_4; Ni + ThO_2 + kieselguhr (200°) C_3H_8; Ni + Al_2O_3 + kieselguhr (165°) $Pr^{\beta}OH$, CH_4; Ni + Al_2O_3 (1:5) (200°), Cu + Al_2O_3 (1:5) (200°), or Ni + TiO_2 (230°) $COMeBu^{\beta}$, $COBu^{\beta}_2$. F. L. U.

Photo-decomposition of gaseous acetone.—See A., 1941, I, 480.

Keto-ethers. VIII. Preparation of γ-chloro-α-ethoxypropyl alkyl ketones. R. C. Wilson with H. R. Henze (*J. Amer. Chem. Soc.*, 1941, **63**, 2112—2113; cf. A., 1939, II, 403).—CH_2:CH·CHO and HCl–EtOH give $Cl·[CH_2]_2·CHCl·OEt$ (66%), b.p. 64—65°/18 mm., converted by AgCN (not CuCN) in Et_2O into *γ-chloro-α-ethoxybutyronitrile* (70%), b.p. 68—70°/3 mm., which with MgRBr in Et_2O gives 40—75% of *Me*, b.p. 68°/4 mm., *Et*, b.p. 86—87°/8 mm., Pr^{α} (I), b.p. 95—96°/6 mm., Pr^{β}, b.p. 90—91°/8 mm., Bu^{α} (II), b.p. 96—98°/4 mm., Bu^{β}, b.p. 94—95·5°/5 mm., *CHMeEt*, b.p. 90—91°/4 mm., n-, b.p. 112—113°/6 mm., and iso-*amyl*, b.p. 98—100°/5 mm., *γ-chloro-α-ethoxy*-n-*propyl ketone*. Of these ketones, only (I) and (II) give *semicarbazones* [m.p. 130° (corr.; decomp.) and 104° (corr.; decomp.), respectively]. Physical consts. of the products are given. R. S. C.

Anomalous reactions of α-bromo-ketones. II. Methyl α-bromohexyl ketone. T. I. Temnikova and V. I. Veksler (*J. Gen. Chem. Russ.*, 1941, **11**, 3—8).—$COMe·C_6H_{13}$-*n* in CCl_4 and Br yield *Me α-bromohexyl ketone*, b.p. 92—92·5°/11 mm. [*semicarbazone*, m.p. 116—118° (decomp.)], which with KOAc or KOBz in EtOH (4—12 hr. at the b.p.) affords *γ-acetoxy-*, b.p. 109—110°/11 mm., or *γ-benzoyloxy-β-keto-octane*, b.p. 148·5—149·5°/1·5 mm. With MgMeBr in Et_2O these esters yield *β-methyloctane-βγ-diol*, b.p. 119—120°/12 mm. R. T.

Structure of diketen from spectroscopic evidence. M. Calvin, T. T. Magel, and C. D. Hurd (*J. Amer. Chem. Soc.*, 1941, **63**, 2174—2177).—Absorption spectra of ββδ-trimethylpentane solutions of diketen (I), β-butyrolactone, CH_2:CH·OAc, and dehydroacetic acid show that the most probable structure of (I) is  with easy transformation into CHAc:CO. W. R. A.

Acyl exchanges between esters and 1:3-diketones and β-keto-esters. S. M. McElvain and K. H. Weber (*J. Amer. Chem. Soc.*, 1941, **63**, 2192—2197).—The reaction $RCO_2R' + COR''·CHNa·COR''' \rightarrow COR''·CHNa·COR + R'''CO_2R'$ is effected by heating the pure enolate and ester with continuous removal of the more volatile constituent (20° rise of temp.); interaction is incomplete owing to solidification of the product; formation of some R'OH indicates presence of $ONa·CR(OR')·CH(COR'')·COR'''$ as intermediate. The similar exchange, $COR·CR'Na·CO_2R''$ (*A*) + $R'''CO_2Et \rightarrow COR'''·CR'Na·CO_2R'' + RCO_2Et$, is more facile and has preparative val.; an intermediate of the type, $COR'''·CH_2·C(ONa)(OEt)·CHR'·CO_2R''$ [from (*A*; R = Me)], is probable. COPh·CHNa·COMe with EtOBz at 150° gives EtOAc (49) and CH_2Bz_2 (48%), with *p*-$C_6H_4Cl·CO_2Et$ (I) at 145° gives EtOAc (33%), *p*-$C_6H_4Cl·CO·CH_2Bz$, and much *di-p-chlorobenzoylmethane*, m.p. 158—159° [formed by a reversed Tischtschenko reaction; also obtained from (I) by NaOEt at 160—180°], with $CH_2Ph·CO_2Et$ at 150° gives EtOAc (43%), $COPh·CH_2·CO·CH_2Ph$, $CH_2(CO·CH_2Ph)_2$, and EtOBz (40%), and with Et 2-furoate (II) at 140° gives EtOAc (51) and ω-2-furoylmethylacetophenone (47%). $CHAc_2Na$ and (II) at 135° give EtOAc (72), 2-furoylacetone (32), and difuroylmethane (34%). $CHNaBz_2$ does not react with EtOAc at 125° or with (I) at 180°. CHAcNa·CO_2Et and EtOBz at 100—155° give EtOAc (46—56) and CHBz·CO_2Et (33—49%). CEtAcNa·CO_2Et and EtOBz at 140° give EtOAc (10), $Pr^{\alpha}CO_2Et$ (60), and CHBzNa·CO_2Et (61%). *Et* α-iso*butyryl*-n-*butyrate* (III) and EtOBz at 145° give $Pr^{\beta}CO_2Et$ (72) and CHEtBz·CO_2Et (50%). CHAcNa·CO_2Et with (II) at 135° gives EtOAc (66) and Et 2-furoylacetate (38%), and with Et 3-pyridylacetate at 160° gives EtOAc (73), 3-ω-carbethoxyacetylpyridine (4%), and much tar. $CHNa(CO_2Et)_2$ and EtOBz at 135° give Et_2CO_3 (10) and $CH_2Bz·CO_2Et$ (16%). (III), b.p. 105—107°/18 mm., is obtained from $Pr^{\beta}CO_2Et$ and $Pr^{\alpha}CN$ by way of α-iso*butyryl*-n-*butyronitrile*, b.p. 89—90°/11 mm. R. S. C.

Action of hydrogen peroxide in *tert.*-butanol on *d*-glucal and its triacetate in presence of osmium tetroxide. R. C. Hockett, A. C. Sapp, and S. R. Millman (*J. Amer. Chem. Soc.*, 1941, **63**, 2051—2053).—*d*-Glucal triacetate, 2—3 mols. (1 mol. causes incomplete reaction) of 5·63% H_2O_2–$Bu^{\gamma}OH$, and a trace of OsO_4 give 55—60% of *d*-glucose (I) (isolated as *β-d*-glucose penta-acetate), a trace of mannose (II), and 5% of volatile acids (III). *d*-Glucal gives similarly (1—2 mols. of H_2O_2) (I) (8—18%), (II) (2%), and (III) (8%). R. S. C.

***D*-Galactosan<1:5>β<1:3>, a new anhydride of *D*-galactose.** R. M. Hann and C. S. Hudson (*J. Amer. Chem. Soc.*, 1941, **63**, 2241—2242).—Pyrolysis (cf. A., 1941, II, 242) of α-*D*-galactose gives *D-galactosan*<1:5>β<1:3> (I), m.p. 174—175° (corr.), $[\alpha]_D^{20}$ +54·9° in H_2O, and a small amount of *D*-galactosan<1:5>β<1:6> (isolated as CMe_2: derivative). The structure of (I) is proved by formation of a 2:4:6-*triacetate*, m.p. 79—80° (corr.), $[\alpha]_D^{20}$ +144·9° in $CHCl_3$ (correct mol. wt. in camphor), failure to react with Fehling's solution or $NaIO_4$, and hydrolysis by 0·2N-HCl at 100° (not 20°) to *D*-galactose. R. S. C.

Isolation of crystalline cardiac glucoside from *Adonis vernalis* and its identification as cymarin.—See A., 1941, III, 819.

Synthesis of glucosido-2-glucose. A. M. Gachokidze (*J. Gen. Chem. Russ.*, 1941, **11**, 117—126).—1-Chloroglucose 3:4:6-triacetate in Et_2O and AgOAc yield *glucose* 1:3:4:6-*tetra-acetate*, m.p. 138°, a solution of which in $CHCl_3$ when shaken with glucose 2:3:4:6-tetra-acetate and $ZnCl_2$ affords glucosido-2-glucose 2′:3′:4′:6′:1:3:4:6-octa-acetate (I), hydrolysed by NaOMe in MeOH to (1:5)-glucosido-2-(1:5)-glucose (*phenylhydrazone*, m.p. 178°). This is oxidised by aq. Br to *glucosido-2-gluconic acid*, a syrup, which is methylated (Me_2SO_4) to *Me* 2:3:4:6-*tetramethylglucosido*-α-(1:3:4:6-*tetramethyl*)*gluconate*, a syrup, $[\alpha]_D$ +95·9° in $CHCl_3$. (I) is heated with NH_2OH in EtOH and the solution is evaporated to a syrup, which is heated at 110° with NaOAc and

Ac_2O, yielding *glucosido-2-gluconitrile* 2′ : 3′ : 4′ : 6′ : 1 : 3 : 4 : 6-*octa-acetate*, m.p. 149—151°. This is heated with NaOEt in EtOH, the solution is diluted with H_2O, extracted with $CHCl_3$, and the extract is shaken with AgOAc in Ac_2O, yielding glucosido-2-arabinoside (*Ac*$_8$ derivative, m.p. 168—180°, $[\alpha]_D$ −21·5° in $CHCl_3$). R. T.

Glucosides of the œstrone series. A. Hagedorn, F. Johannessohn, E. Rabald, and H. E. Voss (*Z. physiol. Chem.*, 1940, **264**, 23—30; cf. A., 1939, II, 358).—Acetobromoglucose (I), œstrone (II), and 2N-KOH in $COMe_2$ at room temp. for 12 hr. give 10% of *œstrone glucoside tetra-acetate*, m.p. 214°, $[\alpha]_D^{17}$ +64·64° in $CHCl_3$ [also obtained in 63% yield from (I), (II), and Ag_2CO_3 in quinoline at 60°], which when reduced (H_2, PtO_2, EtOH) affords *œstradiol glucoside*, m.p. 234°. The physiological activity of these and related compounds is studied (see A., 1941, III, 1010.) H. B.

Polysaccharides synthesised by *Streptococcus salivarius* and *S. bovis*.—See A., 1941, III, 804.

Synthesis of *N*-substituted choline carbamates and trimethyl-β-anilinoethylammonium chloride. D. B. Sprinson (*J. Amer. Chem. Soc.*, 1941, **63**, 2249—2251).—$ClCO_2{\cdot}[CH_2]_2{\cdot}Cl$ (1 mol.) with the appropriate amine (2 mols.) in C_6H_6 or amine hydrochloride (1 mol.) and Na_2CO_3 (1·05 mol.) in H_2O at <0° gives β-chloroethyl methyl-, b.p. 100—102°/11 mm., *dimethyl-*, b.p. 80—81°/9 mm., ethyl-, b.p. 102—104°/11 mm., *diethyl-*, b.p. 66—68°/1 mm., *n*-propyl-, b.p. 83—85°/1 mm., n-*butyl-*, b.p. 97—99°/1 mm., *pentamethylene-*, b.p. 91—93°/2 mm., and -phenyl-carbamate, b.p. 133—135°/2 mm. With NaI in dry $COMe_2$ or MeOH at <0° these give *β-iodoethyl dimethyl-*, b.p. 109—110°/4 mm., n-*propyl-*, m.p. 50°, b.p. 98°/0·07 mm., n-*butyl-*, m.p. 46°, b.p. 106—108°/0·07 mm., *pentamethylene-*, b.p. 115—117°/2 mm., and *phenyl-carbamate*, m.p. 77—79°. The chloroethyl carbamates with NMe_3 at 50—70°, usually in $COMe_2$, give trimethyl-β-methyl-, m.p. 178—180° (corr.) (lit. 171—173°), *-dimethyl-*, m.p. 185—187° (corr.), *-ethyl-*, m.p. 198—200° (corr.), and *-diethyl-*, m.p. 131—133° (corr.), *-carbamylethylammonium chloride*. The I-compounds at room temp. give similarly *trimethyl-β-diethyl-*, m.p. 121—123° (corr.), -n-*propyl-*, softens at 85—87°, m.p. 87—89° (corr.), -n-*butyl-*, m.p. 101—103° (corr.), *-pentamethylene-*, m.p. 200—201° (corr.), and *-phenyl-*, m.p. 131—132° (corr.), *-carbamylethylammonium iodide*. *Triethyl-β-diethyl-*, m.p. 99—101° (corr.), and *-pentamethylene-carbamylethylammonium iodide*, m.p. 95—97° (corr.), are similarly obtained, but
$NHPh{\cdot}CO_2{\cdot}[CH_2]_2{\cdot}I$ and NEt_3 in $COMe_2$, even at −10° to −5°, give NEt_3,HI and 3-phenyloxazolid-2-one.
$NHPh{\cdot}[CH_2]_2{\cdot}Cl$ was not obtained from $NHPh{\cdot}[CH_2]_2{\cdot}OH$ by $SOCl_2$; its *hydrochloride*, m.p. 157—159°, with NMe_3 in $COMe_2$ at room temp. and later 70—75° gives *β-anilinoethyltrimethylammonium chloride hydrochloride*, m.p. 221—222° (corr.; dec. comp.). *N*-Substitution of choline carbamate abolishes the muscarine, but does not affect the stimulating nicotine, activity. R. S. C.

Aryl and alkyl ethers of β-methylcholine. A. R. Goldfarb (*J. Amer. Chem. Soc.*, 1941, **63**, 2280—2281).—Passage of $NHMe_2$ into propylene oxide and MeOH at 60° gives *β-dimethylamino*iso*propyl alcohol* (70%), b.p. 124·5—126°/758 mm., converted by $SOCl_2$ in $CHCl_3$ at −5° to 0° into the cryst. *chloride hydrochloride* (>70%), which with anhyd. NaOR (2·2 mols.) in ROH or NaOMe–MeOH–ArOH at 100° gives *dimethyl-β-methoxy-*, b.p. 113—116° (*methiodide*, m.p. 155·5—156°), *-ethoxy-*, b.p. 133—135° (*methiodide*, m.p. 144·5°), -iso*propoxy-*, b.p. 140—145°/758 mm. (*methiodide*, m.p. 145·5°), -n-*butoxy-*, b.p. 55—58°/18 mm. (*methiodide*, m.p. 156·5—157°), *-phenoxy-*, b.p. 143—144°/18 mm. (*methiodide*, m.p. 139·5—140°), -o-, b.p. 132—135°/18 mm. (*methiodide*, m.p. 141—142°), -m-, b.p. 136—140°/12 mm. (*methiodide*, m.p. 130—131°), and -p-*tolyloxy-*, b.p. 140—143°/15 mm. (*methiodide*, m.p. 140—141°), -n-*propylamine*.
$OH{\cdot}CHMe{\cdot}CH_2{\cdot}NEt_2$ (modified prep.), b.p. 62·5—63·5°/22 mm., gives similarly the *chloride hydrochloride* and thence *diethyl-β-methoxy-*, b.p. 46—47°/12 mm., *-ethoxy-*, b.p. 70—72°/18 mm', -iso*propoxy-*, b.p. 60—63°/10 mm. (*ethiodide*, m.p. 129—130°), -n-*butoxy-*, b.p. 63—65°/10 mm., *-phenoxy-*, b.p. 125—126°/11 mm., -o-, b.p. 141°/12 mm. (*ethiodide*, m.p. 128°), -m-, b.p. 141—142°/10 mm. (*ethiodide*, m.p. 129—130°), and -p-*tolyloxy-*, b.p. 144—146°/14 mm. (*ethiodide*, m.p. 138—139°), -n-*propylamine*. R. S. C.

Production and properties of additive compounds of amino-acids with sugars. A. Kuzin and O. Poljakova (*Biochimia*, 1941, **6**, 113—121).—In conc. solutions at alkaline reaction, NH_2-acids yield additive compounds, isolated as Ca and Ba salts, with monosaccharides. The compounds, which readily hydrolyse in acid and neutral media, are of the *N*-glucoside type. W. McC.

Ammonolysis. II. Ammonolysis of α-halogeno-acids in liquid ammonia. H. H. Sister and N. D. Cheronis (*J. Org. Chem.*, 1941, **6**, 467—478; cf. A., 1941, II, 243).—For all except very high mol. ratios of acid to NH_3 the yield of glycine (I) from $CH_2Cl{\cdot}CO_2H$ and NH_3 is < that from the reaction in aq. NH_3 using the same mol. ratio. The extent of conversion into (I) remains practically const. in the anhyd. system until the ratio acid : NH_3 is decreased to >0·05, whereas in aq. NH_3 a steady rise in % conversion with decreasing ratio of acid : NH_3 is obtained throughout. The yield of (I) is definitely increased by use of 2 mols. of an NH_4 salt and there is a further increase when 4 mols. are used. 6 mols. of NH_4NO_3 produce no further increase, whilst 6 mols. of NH_4Cl cause only a slightly larger effect than 4 mols. The effect of 2 mols. of NH_4NO_3 is confirmed by observations with $CH_2Br{\cdot}CO_2H$ and $CHMeCl{\cdot}CO_2H$. Appreciable increase in the yield of (I) is not caused by the presence of NaCl or $NaNO_3$, showing that the effect is not due to electrolytes in general but to NH_4^+. Liquid NH_3 is more basic than H_2O and hence has a higher affinity for protons, thus favouring the existence of the ion $NH_2{\cdot}CHR{\cdot}CO_2^-$ (*A*) rather than the zwitterion $^+NH_3{\cdot}CHR{\cdot}CO_2^-$ (*B*). Since (*B*) has a free pair of electrons on N it is open to further reaction with the halogen compound, thus leading to the formation of *sec.* and *tert.* ammonolytic products. If, however, $[NH_4^+]$ is very high the equilibrium is somewhat forced from (*B*) towards (*A*), thus reducing (*B*) concn. and inhibiting the *sec.* and *tert.* ammonolytic changes. NH_4 salts are acids in liquid NH_3 and their effect on the ammonolysis of halogen acids in liquid NH_3 is analogous to the p_H effect observed in aq. systems. The pronounced increase in % conversion by $NH_2{\cdot}CO_2NH_4$ is difficult to explain. Experiments with $CH_2Br{\cdot}CO_2H$, $CHMeBr{\cdot}CO_2H$, $CHEtBr{\cdot}CO_2H$, $CHPr^{\alpha}Br{\cdot}CO_2H$, and $CHPr^{\beta}Br{\cdot}CO_2H$ show that ammonolysis in liquid NH_3 is more promising with the less reactive acids (II) of higher mol. wt. than with $CH_2Cl{\cdot}CO_2H$, as there is less tendency towards the formation of *sec.* and *tert.* products. With (II) liquid NH_3 is superior to aq. NH_3, since the reaction is faster and temp. may be raised without fear of hydrolytic side reactions. With $CH_2Br{\cdot}CO_2H$ and $CH_2Cl{\cdot}CO_2H$ a change in the ratio acid : NH_3 from 1 : 12 to 1 : 20 does not affect the % conversion into (I). With $CHMeBr{\cdot}CO_2H$ a marked improvement in the yield of NH_2, derivative is obtained with use of 1 : 20 rather than 1 : 12, and a still greater effect is produced with this change of ratio with $CHEtBr{\cdot}CO_2H$. $CHPr^{\beta}Br{\cdot}CO_2H$ gives an 84·5% conversion at a ratio 1 : 8, and an almost quant. conversion at 1 : 20. H. W.

Microscopy of the amino-acids and their compounds; silver salts. K. Inouye, R. Sunderlin, and P. L. Kirk (*Ind. Eng. Chem. [Anal.]*, 1941, **13**, 587—588; cf. A., 1939, II, 470).—Cryst. NH_2-acids dissolved in H_2O, and a small crystal of $AgNO_3$, give cryst. Ag salts. Cryst. form of *Ag* salts of the following is given (nearly all are needles): alanine, arginine, aspartic acid, glutamic acid (I), glycine, histidine (II) (2 forms of Ag salt), hydroxyvaline, *iso*leucine, leucine, norleucine, norvaline, phenylalanine, hydroxyproline, serine, tryptophan, tyrosine (III), and valine [anisotropic with parallel extinction and elongation (−)], and di-chloro-, -bromo-, and -iodotyrosine [elongation (+)]. Characteristic crystals are those from (I), (II), (III), and the dihalogenotyrosines. Cystine, cysteine, lysine, *iso*serine, proline, and methionine do not give Ag salts. A. T. P.

New method for isolating *l*(+)-lysine. A. C. Kurtz (*J. Biol. Chem.*, 1941, **140**, 705—710).—*l*(+)-Lysine is isolated from protein hydrolysates by conversion of the NH_2-acids into their Cu salts by $CuCO_3$,$Cu(OH)_2$, and subsequent benzoylation by BzCl–aq. NaOH at 0°. The ε-benzoyl-*l*-(+)-lysine–Cu complex is decomposed by aq. H_2S to ε-benzoyl-*l*(+)-lysine, m.p. 247—260° (impurities remain in mother-liquor), converted by refluxing with aq. HCl into *l*(+)-lysine dihydrochloride, m.p. 192—193°. Yields of lysine from various proteins are recorded. No insol. derivative is obtained when solutions of arginine–Cu chloride or hydroxyproline–Cu are treated with BzCl–aq. NaOH. A. T. P.

Special lability of serine and threonine towards alkali, when in peptide combination. B. H. Nicolet and L. A. Shinn (*J. Biol. Chem.*, 1941, **140**, 685—686).—Serine and threonine are destroyed by alkali when in peptide combination but not when free. It is suggested that seryl peptide first loses H_2O and is then hydrolysed. E. M. W.

Deuteromethionine and deuterocholine.—See A., 1941, III, 899.

Palmitoyl- and stearoyl-glycylglycine and -diglycylglycine. A. Koebner (*J.C.S.*, 1941, 564—566).—Palmitoylglycine Me ester, m.p. 104—105°, and 5% NH_3–MeOH at room temp. give *palmitoylglycinamide*, m.p. 161—162°. Stearoylglycine, new m.p. 125—126°, affords the Me ester, m.p. 75—76°, and thence the *amide*, m.p. 157—158°. Glycine anhydride and palmitoyl (**I**) or stearoyl chloride (**II**) in 2N-NaOH–Et_2O yield *palmitoyl-*, m.p. 171—172° (decomp.) [and thence (HCl–MeOH) the *Me* ester, m.p. 139°, and (MeOH–NH_3 in sealed tube) *amide*, m.p. 199—200°], or *stearoyl-glycylglycine*, m.p. 168° (softens at 160°) (*Me* ester, m.p. 135—136°; *amide*, m.p. 196°), respectively. Diglycylglycine and (**I**) or (**II**) in 2N-NaOH–Et_2O afford *palmitoyl-*, m.p. 209° (decomp.), or *stearoyl-diglycylglycine*, m.p. 210°, respectively, which have not been esterified. A. T. P.

Formation of betaine from hydroxyamino-acids on methylation. H. D. Dakin (*J. Biol. Chem.*, 1941, **140**, 847—852).—Serine, threonine, *cis-* and *trans*-phenylserine, and hydroxyaspartic (**I**) and hydroxyglutamic acids form varying amounts of betaine on methylation, whereas cystine and cysteine produce considerable quantities of NMe_4·OH. N of (**I**) and, to a smaller extent, the phenylserines is also partly converted into NMe_4 salts. H. G. R.

Stereoisomeric forms of lanthionine. G. B. Brown and V. Du Vigneaud (*J. Biol. Chem.*, 1941, **140**, 767—771; cf. A., 1941, II, 188).—*p*-Nitrobenzoyl-*l*-serine, $[\alpha]_D^{20}$ +43·8° in aq. NaOH, is hydrolysed in 16% HBr and then esterified to *l*-serine Me ester hydrochloride, which is converted into *l*-β-chloro-α-aminopropionic acid hydrochloride (**I**) (free acid, $[\alpha]_D^{20}$ −15° in H_2O). *l*-Cystine when treated with Na in liquid NH_3 and then with aq. KOH under N_2 and (**I**) affords l(+)-*lanthionine* (**II**), decomp. 293—295° (darkens at 245°), $[\alpha]_D^{20}$ +8·6° in dil. NaOH (*Bz_2* derivative, m.p. 202—204°). Benzyl-*d*-cysteine is reduced in liquid NH_3 with Na, and the *d*-cysteine produced is condensed with (**I**) to give d(−)-*lanthionine* (**III**), decomp. 293—295° (darkens at 245°), $[\alpha]_D^{21}$ −8·0° in dil. NaOH (*Bz_2* derivative, m.p. 202—203°). Equal quantities of (**II**) and (**III**) in aq. NH_3 afford dl-*lanthionine*, decomp. 286—292° (darkens at 240°) (*Bz_2* derivative, m.p. 183—184°). The *meso*-form assigned to the inactive isomeride prepared previously (*loc. cit.*) and also by Horn *et al.* (A., 1941, II, 188), is confirmed. A. T. P.

Reaction of arsenic trichloride with diazomethane. G. I. Braz and A. J. Jakubovitsch (*J. Gen. Chem. Russ.*, 1941, **11**, 41—44).—$AsCl_3$ and CH_2N_2 in Et_2O at 0° yield *chloromethylarsine dichloride*, b.p. 57—58°/16 mm., and *di(chloromethyl)-arsine chloride*, b.p. 86—88°/16 mm., from which *chloromethyl-*, sinters at 133—135°, and *di(chloromethyl)-arsinic acid*, m.p. 117—126° (decomp.), are prepared. R. T.

II.—HOMOCYCLIC.

Investigation of the *cyclo*hexane–methyl*cyclo*pentane equilibrium by the Raman effect.—See A., 1941, I, 467.

Dipole moments of some nitro- and amino-derivatives of benzene and naphthalene.—See A., 1941, I, 400.

Preparation of styrene by catalytic dehydrogenation of ethylbenzene. A. A. Balandin, N. D. Zelinski, G. M. Marukian, and O. K. Bogdanova (*J. Appl. Chem. Russ.*, 1941, **14**, 161—172).—Styrene is obtained in 50—55% yield by passing 1 : 2 PhEt–CO_2 or –N_2 mixtures over 1 : 4 Cu–CrO_3 catalyst at 650°, or over 1 : 19 V_2O_5–Al_2O_3 catalyst at 625°. ~15% of the PhEt is used up in side reactions involving production of CH_4, C_2H_6, and C_6H_6. R. T.

Pyrolysis of αaγ-triphenyl-Δ$^{\alpha}$-propene. C. F. Koelsch and P. R. Johnson (*J. Org. Chem.*, 1941, **6**, 534—542).—Pyrolysis of CPh_2:CH·CH_2Ph (**I**) is scarcely observed at 450—460° under reduced pressure, but at atm. pressure the following are produced: PhMe, CPh_2:CH_2, $CHPh_2Me$, CH_2Ph_2, 1 : 2- (**II**) and 2 : 3-diphenylindene (**III**), identified by conversion into pure (**III**) by warming with KOH–EtOH and into 2 : 3-diphenyl-1-benzylideneindene by treatment with PhCHO and alkali. Oxidation (CrO_3) of the oils remaining after removal of the indenes gives BzOH, CH_2Ph·CO_2H, *o*-C_6H_4Bz·CO_2H, $COPh_2$, and *o*-$C_6H_4Bz_2$, indicating the presence of 1 : 3-diphenylindene (**IV**) and (**I**). The distillation residue contains a minute amount of a cryst. material, m.p. 280°, (**II**), and (**III**); oxidation of the non-cryst. remainder gives *o*-$C_6H_4Bz_2$ [indicating (**IV**)], BzOH, and anthraquinone (origin uncertain). Of compounds possible through coupling of radicals formed by cracking during pyrolysis only (**I**) is isolated. This is not regarded as evidence against the formation of free radicals, since coupling between two energy-rich fragments probably requires the assistance of a third body for the dissipation of energy. Further, the concn. of the radicals is low, so that their most likely fate is to become hydrogenated at the expense of the relatively abundant (**I**). Cyclisation of (**I**) probably results from the dehydrogenation of the acyclic hydrocarbon by the free radicals formed through cracking; this hypothesis is supported by a semi-quant. survey of all the pyrolysis products, which shows that a mol. is cyclised for every mol. which is cracked. Direct cyclisation should lead to 1 : 1-diphenylindene, which is not found, or to (**IV**), present only in small amount. The main cyclisation products are (**II**) and (**III**), easily interconvertible substances the formation of which from (**I**) necessitates the migration of Ph. Probably migration occurs after and not before cyclisation, since rearrangement before cyclisation would lead to $CHPh$:CPh·CH_2Ph, and either this substance or its cracking products, stilbene or $(CH_2Ph)_2$, would be isolated. Apparently the breaking of an open propylene chain is more readily effected than is displacement of Ph. To avoid the cleavage, the C chain along which Ph migrates must be part of a ring, and a cyclic structure thus appears essential for this type of rearrangement. Since C_6H_6 is not produced the migrating Ph does not separate as a free radical. H. W.

Attempted synthesis of αβγ-triphenyl-Δ$^{\alpha\gamma}$-butadiene. Synthesis and properties of αβγ-triphenylallyl alcohol. F. Bergmann (*J. Org. Chem.*, 1941, **6**, 543—549).—$CHPh$:CPh·$CHPh$·OH (**I**) is obtained when the product of the action of MgPhBr on $CHPh$:CPh·CHO is decomposed with NH_4Cl, whereas when dil. H_2SO_4 is used and the residue is distilled in vac. 1 : 2-diphenylindene, m.p. 177°, results. (**I**) is also obtained from $Al(OPr^{\beta})_3$ and benzylidenedcoxybenzoin in $Pr^{\beta}OH$ and is converted by boiling Ac_2O into its *acetate* (**II**), m.p. 129°, and by MeOH containing a little conc. H_2SO_4 at room temp. into its *Me ether* (**III**), m.p. 96°. (**II**) and conc. H_2SO_4 afford 2 : 3-diphenylindene. Boiling HI with subsequent distillation under 5 mm. transforms (**I**), (**II**), or (**III**) into 1 : 2-diphenylhydrindene, m.p. 126°. With Na powder in Et_2O (**I**) appears to give a C·Na compound decomposed by EtOH to benzyldeoxybenzoin, m.p. 120°, and the α-form, m.p. 92°, of CH_2Ph·$[CHPh]_2$·OH. This with the β-variety, m.p. 86—89°, is obtained by the reduction (H_2–Pd–$BaSO_4$ in AcOH) of (**I**). (**III**) and Na in Et_2O give the product $CHPh$:CPh·$CHPhNa$ (**IV**), transformed by CH_2O into *βγδ-triphenyl-Δγ-buten-α-ol* (**V**), m.p. 106°, which does not decolorise Br. It could not be satisfactorily dehydrated to $CHPh$:CPh·CPh:CH_2 (**VI**). (**V**) and boiling AcCl give an *acetate*, m.p. 94°, stable at 350°/atm. pressure. When (**V**) is boiled with Na in xylene and the filtered solution is treated successively with CS_2, MeI, and Ag powder, a liquid, b.p. 155°/0·2 mm., results which does not give satisfactory analytical results but may contain (**VI**), since it strongly decolorises Br; it does not give a picrate or an additive compound with maleic anhydride. The structure of (**III**) is established by its conversion by CH_2PhCl into $CHPh$:CPh·$CHPh$·CH_2Ph, m.p. 147—148°. H. W.

Preparation of chloromethylindenes and determination of their reactivities towards sodium iodide. C. F. Koelsch and R. V. White (*J. Org. Chem.*, 1941, **6**, 602—611).—The reactivity of a substituted 2- or 3-chloromethylindene towards NaI exceeds that of an alkyl chloride and lies in the range of reactivities of the substituted benzyl chlorides. Since the rate consts. are so highly dependent on apparently insignificant structural features of the chloromethylindenes, it is not possible to make a precise summarising statement. Gradual addition of Br to α-methylstilbene in AcOH at 60° followed by boiling the mixture gives *α-bromo-αβ-diphenyl-Δ$^{\alpha}$-propene*, b.p. 153—156°/0·001 mm., the Grignard reagent from which is carbonated by solid CO_2 to *αβ-diphenylcrotonic acid*, m.p.

124—126°, which does not appear to be cyclised by $POCl_3$ in C_6H_6. Fluorenone (I) is converted by this Grignard reagent followed by boiling AcOH containing a few drops of conc. H_2SO_4 into *βγ-diphenyl-α-diphenylene-Δ$^{\alpha\gamma}$-butadiene*, m.p. 197—198°, transformed by more prolonged action of AcOH–H_2SO_4 into *2-phenyl-1-diphenylene-3-methylindene* (II), m.p. 152·5—153·5°, oxidised by CrO_3 in AcOH at room temp. to BzOH and diphenylenephthalide, m.p. 220—222°. (II) is transformed by Br in $CHCl_3$ in direct sunlight and subsequent treatment with KOAc in boiling AcOH into *1-diphenylene-2-phenyl-3-acetoxymethylindene*, m.p. 172—173°, which is unchanged by HCl in boiling AcOH but converted by AcOH–conc. HCl at 150° into *2-phenyl-1-diphenylene-3-chloromethylindene*, m.p. 145·5—146·5°. (I) is transformed by the Grignard reagent (III) from CPh_2:CMeBr, b.p. 169—173°/13 mm., into the non-cryst. carbinol, converted by boiling AcOH–H_2SO_4 into *3-phenyl-1-diphenylene-2-methylindene*, m.p. 173—174·5°, which is transformed through the 2-CH_2Br and 2-$OAc{\cdot}CH_2$ compound, m.p. 148·5—150°, into *3-phenyl-1-diphenylene-2-chloromethylindene*, m.p. 134—136°. $COPh_2$ is converted by (III) and subsequent treatment with boiling AcOH–H_2SO_4 into 1 : 1 : 3-*triphenyl-2-methylindene*, m.p. 157—159·5°, oxidised by CrO_3 in hot AcOH to *o*-benzoyltriphenylacetic acid, m.p. 129° (decomp.), and *o-benzoyl-ααα-triphenylacetone*, m.p. 172—173·5°, and transformed by the usual steps into 1 : 1 : 2-*triphenyl-2-bromomethyl-*, m.p. 154—156°, *-2-acetoxymethyl-*, m.p. 178·5—180°, and *-2-chloromethyl-*, m.p. 154—155·5°, *-indene*. spiro-3-*Phenyl-2-methylindene*-1 : 9-*xanthene*, m.p. 153·5—155°, is obtained from (III) and xanthone and converted successively into the *-2-OAc·CH$_2$*, m.p. 203·5—205°, and *-2′-CH$_2$Cl*, m.p. 144—145°, compounds. 1-Bromo-1 : 2 : 3-triphenylindene and MgMeI in boiling Et_2O–C_6H_6 afford *1-methyl-1 : 2 : 3-triphenylindene* (IV), m.p. 96—98°, which with 1 equiv. of Br in AcOH affords a *substance*, $C_{28}H_{21}Br$, m.p. 170—171° after softening at 162°, which fails to react with $AgNO_3$ in EtOH. Triphenylacrylophenone (V) and MgMeI give CPh_2:CPh·CPhMe·OH (VI), m.p. 96—98°, transformed by NaOAc and boiling Ac_2O into *ααβγ-tetraphenyl-Δ$^{\alpha\gamma}$-butadiene*, m.p. 118·5—120°. This is oxidised by powdered $KMnO_4$ in $COMe_2$ to (V) and converted by H_2SO_4–AcOH into (IV), also obtained directly from (VI).

H. W.

Synthesis of growth-inhibitory polyocyclic compounds. III. G. M. Badger (*J.C.S.*, 1941, 535—538).—1- and 2-$C_{10}H_7{\cdot}CHO$ [from $C_{10}H_7{\cdot}CH_2Br$ and $(CH_2)_6N_4$ in boiling AcOH] with 1- and 2-$C_{10}H_7{\cdot}CH_2{\cdot}CO_2Na$ in Ac_2O at 130—140° yield *α-1-naphthyl-β-2-*, m.p. 215—216° (after sintering), *α-2-naphthyl-β-1-* (I), m.p. 213—214° (after sintering), and *αβ-di-1-naphthylacrylic acid*, m.p. 227—228°. (I) with Cu-bronze in quinoline at 240—250° yields *α-1-naphthyl-β-2-naphthylethylene*, m.p. 103—105°. 1-$C_{10}H_7{\cdot}CO{\cdot}CH_2Ph$ with MeI in EtOH–NaOEt yields *1-α-phenylpropionylnaphthalene*, b.p. 172—173°/0·5 mm., which with MgMeI and MgEtI followed by dehydration (PBr_3 in $CHCl_3$) yields respectively *β-phenyl-γ-1-naphthyl-Δ$^{\beta}$-butene*, m.p. 68·5—70° (via *γ-phenyl-β-1-naphthylbutan-β-ol*, m.p. 97—99°), and *-Δ$^{\beta}$-pentene*, b.p. 161—164°/0·6 mm. 2-$C_{10}H_7{\cdot}CO{\cdot}CH_2Ph$ similarly yields *2-α-phenylbutyrylnaphthalene*, m.p. 116—118°, *γ-phenyl-δ-2-naphthyl-Δ$^{\gamma}$-hexene*, b.p. 165—168°/0·5 mm., and *-Δ$^{\gamma}$-pentene*, b.p. 178—180°/1 mm. Fluorene and 1 : 2-benz- and 1 : 2 : 5 : 6-dibenz-fluorene are oxidised (SeO_2 in H_2O at 230—240°) to fluorenone (II) and 1 : 2-benz- (III) and 1 : 2 : 5 : 6-*dibenz-fluorenone*, m.p. 164—165°, respectively. (II) and (III) with MgMeI yield respectively 9-methyl-fluoren-9-ol and *-1 : 2-benzfluoren-9-ol*, m.p. 170·5—171·5°, dehydration (boiling AcOH) and hydrogenation (PtO_2) of which yields 9-methyl-fluorene and *-1 : 2-benzfluorene*, m.p. 120·5—122·5° (*bis*-s-*trinitrobenzene* complex, m.p. 109—111°).

A. Li.

Cyclisation of dienines. XI. Ring closures with di-Δ^2-octahydro-2-naphthylacetylenes. Synthesis of perhydro-9-phenanthrone. C. S. Marvel and L. A. Paterson (*J. Amer. Chem. Soc.*, 1941, **63**, 2218—2220; cf. A., 1941, II, 15).—The Grignard reagent of 2-hydroxy-2-acetylenyl-*trans-* and *-cis*-decahydronaphthalene with 2-keto-*trans*-decahydronaphthalene gives 2 : 2′-*dihydroxydi*-trans-*decahydronaphthylacetylene*, m.p. 151·5—152·5°, and the cis–trans-*isomeride*, m.p. 136·5—137°, dehydrated to *di*-Δ^2-trans-*octahydronaphthylacetylene* (I), m.p. 80—82°, and the cis–trans-*isomeride* (II), b.p. 211°/3 mm., respectively. Cyclisation of (I) gives a glassy *product* (III), $C_{22}H_{32}O$, and a trace of a substance, m.p. 112—115°; that of (II) gives a *product* (IV), b.p. 225—245°/6 mm. Dehydrogenation of (III) or (IV) gives a small amount of the hydrocarbon, $C_{22}H_{18}$, m.p. 179—181°, but other derivatives could not be obtained. *o*-$CO_2H{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO_2Me$-*o*, $SOCl_2$, and a little C_5H_5N in C_6H_6 at 45—50° give the *Me* ester *chloride*, m.p. 63—64°, converted by CH_2N_2 and then Ag_2O–MeOH into *Me$_2$ diphenyl-2-carboxylate-2′-acetate*, m.p. 71—71·5°. The derived (10% NaOH) *dicarboxylic acid*, m.p. 171—172°, is hydrogenated (Raney Ni; 215°/2000 lb.) as Na_2 salt in H_2O to *2-carboxyhexahydrodiphenyl-2′-acetic acid*, m.p. 261—263°, and then to a glassy H_{12}-acid, cyclised at 200°, later 300—320° (CO_2), to the known 9-ketotetradecahydrophenanthrene, m.p. 57° (oxime, m.p. 218—219·5°).

R. S. C.

2-Nitro-2′-aminodiphenyl. D. Purdie (*J. Amer. Chem. Soc.*, 1941, **63**, 2276).—(*o*-$NO_2{\cdot}C_6H_4)_2$ and boiling aq. EtOH–Na_2S_x give *2-nitro-2′-aminodiphenyl*, m.p. 94—95° [Ac derivative, m.p. 159—160° (lit. 158°)].

R. S. C.

***p*-Dialkylaminoalkylaminobenzenesulphonamides.**—See B., 1941, **III**, 296.

Synthesis of lipophilic chemotherapeutieals. V. N^4-Acylsulphanilamides. F. Bergmann and L. Haskelberg (*J. Amer. Chem. Soc.*, 1941, **63**, 2243—2245).—*p*-$NH_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH_2$ (I) with RCOCl in C_5H_5N–$CHCl_3$ at 0° (later, room temp.) or NaOAc–AcOH–H_2O at −5° (later, room temp.) gives N^4-*chloroacetyl-*, m.p. 214°, *-dichloroacetyl-*, m.p. 218°, *-trichloroacetyl-*, m.p. 205°, *-bromoacetyl-*, m.p. 218° (decomp.), *-trichloroacryl-*, m.p. 258°, -stearyl-, m.p. 245° (lit. 201°), *-oleyl-*, m.p. 204°, *-Δ^9-octadecinenoyl-* (*-stearolyl-*), m.p. 189°, *-undecoyl-*, m.p. 205° (decomp.), *-undecenoyl-*, m.p. 194—196°, *-dibromoundecoyl-*, m.p. 173—175°, *-cinammoyl-*, m.p. 255—257°, -trans-*αβ-dibromocinnamoyl-*, m.p. 266°, and *-phenylpropiolyl-*, m.p. 254°, N^{4}N$^{4'}$-iso*phthalyldi-*, m.p. >360°, N^{4}N$^{4'}$-*adipyldi-*, m.p. >300°, and N^{4}N$^{4'}$-*sebacyldi-*, m.p. >300°, *-sulphanilamide*. The acid anhydride and (I) at 150° give N-p-*sulphamyl-phthal-*, m.p. 338°, *-tetrachlorophthal-*, decomp. 322°, and -succin-anilic acid, m.p. 212·5—213·5°. p-*Sulphamyldiphenanilic acid*, m.p. 278—279° (decomp.), is obtained from (I) and $(\cdot C_6H_4{\cdot}CO)_2O$ in boiling PrOH (not alone at 150°). Citraconic anhydride and (I) at 25°, later 100°, give p-*citraconimidobenzenesulphonamide*, m.p. 210—213°. Stearolyl chloride, b.p. 210°/15 mm., CPh:C·COCl, b.p. 103—105°/3·5 mm., and *trans*-CPhBr:CBr·COCl, b.p. 205—208°/7 mm., are prepared by $SOCl_2$.

R. S. C.

Preparation of xylidinesulphonamides and of xylidinesulphonyl derivatives of 2-aminopyridine. A. J. Savitzki and E. I. Rodionovskaja (*J. Gen. Chem. Russ.*, 1940, **10**, 2091—2094).—1 : 3 : 4-$C_6H_3Me_2{\cdot}NHAc$ and $ClSO_3H$ (1 hr. at 80°) yield *4-acetamido-m-xylene-6-sulphonyl chloride*, m.p. 133—134° (decomp.), which with aq. NH_3 affords the *-sulphonamide*, m.p. 258—259° (corresponding 4-NH_2-compound, m.p. 187—188°), and with 2-aminopyridine gives 2-(4′-*acetamido-m-xylene-6′-sulphonamido*)*pyridine*, m.p. 260·5—261° (corresponding 4-NH_2-compound, m.p. 244—245°). *2-Amino-*, m.p. 189—190°, and *2-acetamido-*p-*xylene-5-sulphonamide*, m.p. 242—243°, and 2-(2′-*amino-*, m.p. 217—218° (decomp.), and 2-(2′-*acetamido-*p-*xylene-5′-sulphonamido*)*pyridine*, m.p. 243·5—244·5°, were prepared similarly from 2 : 1 : 4 : 5-$NHAc{\cdot}C_6H_2Me_2{\cdot}SO_2Cl$.

R. T.

Synthesis of lipophilic chemotherapeuticals. VI. Lipophilic substitutions in azo-dyes. E. Bergmann, L. Haskelberg, and F. Bergmann (*J. Amer. Chem. Soc.*, 1941, **63**, 2245—2248).—Treatment of the dye with, usually, RCOCl in C_5H_5N–$CHCl_3$ at 0° or boiling K_2CO_3–C_6H_6 gives *acet-*, m.p. 241°, *chloro-*, m.p. 221°, *dichloro-*, m.p. 214°, and *trichloro-acet-* (I), m.p. 153·5°, *trichloroacryl-*, m.p. 143—144°, *undeco-*, m.p. 150°, *undeceno-*, m.p. 84°, *dibromoundeco-*, m.p. 111—112°, *cinnam-*, m.p. 236—237°, *phenylpropiol-*, m.p. 221°, trans-*αβ-dibromocinnam-*, m.p. 215°, *toluenesulphon-*, m.p. 209°, N^4-*acetylsulphanil-* (II), m.p. 270°, *-4-benzeneazo-1-naphthylamide*. *Phthal-*, m.p. 224—225°, and *tetrachlorophthal-4-benzeneazo-1-naphthylimide*, m.p. 296°, are obtained by the anhydride at 120° and 100—130°, respectively. The following are also prepared. *Di-*, m.p. 214°, and *tri-chloroacet-*, m.p. 130°, *trichloroacryl-*, m.p. 174°, *undeceno-*, m.p. 82—84°, *undeco-*, m.p. 98°, *phenylpropiol-*, m.p. 170°, and N^4-*acetylsulphanil-* (III), m.p. 206—207°, *-1-benzeneazo-2-naphthylamide*; 1-*o*-$C_6H_4Cl{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2$-2, m.p. 158° (lit. 151°) (*CCl_3·CO* derivative, m.p. 171°, and +*x*BuOH, m.p. 133°); 1-*p*-carboxy-, m.p. 265° (*CCl_3·CO* derivative, m.p. 246°), 1-*carbethoxy-*, m.p. 183° [*CCl_3·CO* (IV), m.p. 206°, *$C_{10}H_{19}$·CO*, m.p. 106°, *$C_{10}H_{21}$·CO*, m.p. 110—111°, *$C_{10}H_{19}Br_2$·CO*, m.p. 124°, and *CCl_2:CCl·CO*

derivative, m.p. 193°], and 1-p-*carbamyl-benzeneazo-2-naphthylamine*, m.p. 243—244° [*CCl*$_3$·*CO* derivative, m.p. 230° (decomp.)]; 4-*o*-$C_6H_4Cl{\cdot}N_2{\cdot}C_{10}H_6{\cdot}NH_2$-1, m.p. 141° (lit. 129°); 4-p-*carbethoxybenzeneazo-1-naphthylamine*, m.p. 164° (*CCl*$_3$·*CO*, m.p. 149°, and *undecenoyl* derivative, m.p. 164—165°); *trichloroacet*-4-p-*chlorobenzeneazo-1-naphthylamide*, m.p. 184°; 4 : 3 : 1-$NH_2{\cdot}C_6H_3Me{\cdot}N_2Ph$, m.p. 101° (lit. 118—119°); 4-*trichloroacetamido-azobenzene*, m.p. 149°, -2-*methylazobenzene*, m.p. 137°, and -3-*methoxyazobenzene*, m.p. 132°. Hydrolysis of (**II**) regenerates the basic dye, but boiling 15% HCl–EtOH converts (**III**) into *sulphanil-1-benzeneazo-2-naphthylamide*, m.p. 221—222°. (**I**) and (**IV**) are definitely active against leprosy in hamsters and (**I**) for tuberculosis in guinea-pigs.
R. S. C.

p-Aminodimethylaniline. I. Properties of its diazonium compounds. E. E. Ayling, J. H. Gorvin, and L. E. Hinkel (*J.C.S.*, 1941, 613—620).—Diazotisation of *p*-$NH_2{\cdot}C_6H_4{\cdot}NMe_2$ proceeds slowly but quantitatively below 5°, and solutions of *p*-$NMe_2{\cdot}C_6H_4{\cdot}N_2Cl$ (**I**) are stable at p_H <3·5 (the stability, measured by the incipient decomp. temp., decreases with increasing p_H) but are rapidly decomposed by Cu-bronze in the cold (whereby $NPhMe_2$ is formed). Coupling reactions with amines are very slow, the yield being almost independent of p_H or temp. Coupling with phenols is best at low temp. and at a p_H just high enough to give a conveniently rapid rate of reaction. The yields of azo-compounds depend mainly on the substance coupled. (**I**) behaves normally with CuCl and KI.
A. Li.

Oxidation of hydrocarbons to phenols.—See B., 1941, II, 373.

Effect of temperature and light on 2 : 6-dichlorophenol-indophenol solutions. W. Lojander (*Suomen Kem.*, 1941, **14, A**, 26).—The solutions (0·0005—0·001M.) are practically unchanged after 2 months at 6° in the dark, and are only slightly decomposed after 1 month at 20° in daylight and artificial light, but at 30° they are appreciably decomposed after 10 days in the dark.
M. H. M. A.

Aquo-ammonophosphoric acids. I. Preparation of phenyl esters of amido- and diamido-phosphoric acids. L. F. Audrieth and A. D. F. Toy (*J. Amer. Chem. Soc.*, 1941, **63**, 2117—2119).—The products formed from $POCl_3$, PhOH, and C_5H_5N in $CHCl_3$ depend on the mol. ratios of the constituents and on temp. A complex equilibrium is established and ammonolysis gives mixtures of Ph diamidophosphate (**I**), Ph_2 amidophosphate (**II**), and Ph_3PO_4. (**I**) and (**II**) are readily separable and this procedure is recommended for their prep.
W. R. A.

Synthetic œstrogenic substances. II. Hexœstrol and its esters. E. L. Foreman and C. O. Miller (*J. Amer. Chem. Soc.*, 1941, **63**, 2240).—(*p*-$OH{\cdot}C_6H_4{\cdot}CHEt)_2$ (**I**) (prep. from the Me_2 ether improved) and $(RCO)_2O$ in boiling C_5H_5N give the *dipropionate*, m.p. 127—128°, *dibutyrate*, m.p. 106—107°, *dibenzoate*, m.p. 236—237°, *di*-n-*hexoate*, m.p. 96—97°, and *H*$_2$ *disuccinate* (**II**), m.p. 150—153°. The oil-sol. esters have low but prolonged œstrogenic effect. The activity of (**II**) in aq. solution is about the same as that of (**I**).
R. S. C.

4 : 4′-Dihydroxystilbene and related compounds.—See B., 1941, II, 372.

Antimonial and thioantimonial derivatives of pyrocatechol. H. P. Brown and J. A. Austin (*J. Amer. Chem. Soc.*, 1941, **63**, 2054—2055).—*o*-$C_6H_4(OH)_2$ (**I**), $SbCl_3$, and Na_2CO_3 in aq. NaCl give the *hydroxide* (**II**), *o*-$C_6H_4\langle{}^{O}_{O}\rangle Sb{\cdot}OH$ (70%), unchanged at 300°. SbF_3 and (**I**) in H_2O give the *fluoride*, *o*-$C_6H_4\langle{}^{O}_{O}\rangle SbF$ (55%), converted into (**II**) by Na_2CO_3. Moist (**II**) and *o*-$SH{\cdot}C_6H_4{\cdot}CO_2Na$ in H_2O give the *salt* (**III**), *o*-$C_6H_4\langle{}^{O}_{O}\rangle Sb{\cdot}S{\cdot}C_6H_4{\cdot}CO_2Na$-*o*, m.p. >300°, decomposed by acid. *o*-, *m*-, and *p*-$OH{\cdot}C_6H_4{\cdot}CO_2H$ give similarly *salts*, *o*-$C_6H_4\langle{}^{O}_{O}\rangle Sb{\cdot}O{\cdot}C_6H_4{\cdot}CO_2Na$-*o*, -*m*, and -*p*, all m.p. >300°, decomposed by acid. *o*-$C_6H_4(SH)_2$ (**IV**) with SbF_3 in H_2O gives *trisdithiopyrocatecholdistibine*, $(o\text{-}C_6H_4S_2)_3Sb_2$, unchanged at 250°, but with $SbCl_3$ or $SbBr_3$ in boiling C_6H_6 gives *salts*, *o*-$C_6H_4S_2SbCl$, m.p. 174—175° (decomp.), or *o*-$C_6H_4S_2SbBr$, m.p. 162—163° (decomp.), respectively, and with Sb_2O_3 in boiling EtOH gives the corresponding *hydroxide*, m.p. >300°, but with *o*-$OH{\cdot}C_6H_4{\cdot}CO_2Na$ etc. gives indefinite products. K SbO tartrate and (**IV**) in aq. EtOH give the *acid*, *o*-$C_6H_4S_2$>$Sb{\cdot}O{\cdot}CH(CO_2H){\cdot}CH(OH){\cdot}CO_2H$ (K_1 salt, m.p. >250°). *o*-$OH{\cdot}C_6H_4{\cdot}SH$ and freshly pptd. Sb_2O_3 in boiling EtOH give the *compound*, *o*-$C_6H_4\langle{}^{O}_{S}\rangle Sb{\cdot}S{\cdot}C_6H_4{\cdot}OH$-*o*, m.p. >250°, but other derivatives could not be obtained. (**III**) is a useful agent for the treatment of heartworms in dogs.
R. S. C.

Choline tolyl ethers. A. R. Goldfarb (*J. Amer. Chem. Soc.*, 1941, **63**, 2280).—Addition of 50% NaOH (1 mol.) to cresol (1 mol.) and $C_2H_4Br_2$ (2 mols.) in boiling H_2O gives β-o-, b.p. 142—145°/18 mm., -m-, b.p. 146·5—147°/18 mm., and -p-*tolyloxyethyl bromide*, b.p. 136—138°/18 mm., converted by NMe_3 (at 40°) or NEt_3 (at 60°) in PhMe into β-o-, m.p. 157·5°, -m-, m.p. 145·4°, and -p-*tolyloxyethyltrimethyl-*, m.p. 144°, β-o-, m.p. 152—152·5°, -m-, m.p. 136·4°, and -p-*tolyloxyethyltriethyl-*, m.p. 134·5°, *-ammonium bromide*.
R. S. C.

Direct synthesis of many-membered ring compounds from two ωω′-difunctional molecules. R. Adams and L. N. Whitehill (*J. Amer. Chem. Soc.*, 1941, **63**, 2073—2078).—The effect of dilution on interaction of two ωω′-difunctional mols. is discussed. High-dilution technique is used in cyclisations described below. Quinol (**I**), $Br{\cdot}[CH_2]_3{\cdot}Br$, and K_2CO_3 in boiling aq. $COMe_2$ give *quinol di-γ-bromopropyl ether* (**II**) (28·9%), m.p. 78—79°, b.p. 174—177°/4 mm., which (2 mols.) with (**I**) (1 mol.) and KOH (0·3 mol.) in boiling EtOH gives α-p-*hydroxyphenoxy-γ-*p-*γ′-bromo-*n-*propoxyphenoxypropane* (23·7%), m.p. 100—101°, cyclised by addition to K_2CO_3 in boiling *iso*-$C_5H_{11}{\cdot}OH$ to 1 : 1′ : 4 : 4′-*bistrimethylenedioxydibenzene*, *p*-$C_6H_4\langle{}^{O{\cdot}[CH_2]_3{\cdot}O}_{O{\cdot}[CH_2]_3{\cdot}O}\rangle C_6H_4$-*p* (**III**) (59·2%), m.p. 195—195·5°. Direct intermol. condensation of (**I**) and (**II**) to (**III**) is also effected, yields up to 18% being recorded. $Br{\cdot}[CH_2]_6{\cdot}Br$ and (**I**) give similarly *quinol di-ζ-bromo-*n-*hexy ether* (63·2%), m.p. 96—97°, and thence 1 : 1′ : 4 : 4′-*bishexamethylenedioxydibenzene* (15%), m.p. 141°. Attempts to condense quinol di-β-bromoethyl, m.p. 114°, b.p. 145—147°/2 mm., and the insol. *di-κ-bromo-*n-*decyl*, m.p. 88·5—89·5°, and *di-θ-bromo-*n-*octyl ether*, m.p. 78·5—79·5°, with (**I**) failed. Quinol mono-θ-bromo-*n*-octyl ether, m.p. 76—77°, is also described. M.p. are corr.
R. S. C.

Synthesis of 5-methoxy-10-methyl-1 : 2-benzanthracene and related compounds. M. S. Newman and P. H. Wise (*J. Amer. Chem. Soc.*, 1941, **63**, 2109—2111).—*o*-$OMe{\cdot}C_6H_4{\cdot}MgBr$ (**I**) and 1 : 2-$C_{10}H_6(CO)_2O$ in boiling C_6H_6–Et_2O give 13% each of o-*anisyl* 1-*carboxy*-2- (**II**), m.p. 193·8—194·6°, and 2-*carboxy*-1-*naphthyl ketone* (**III**), m.p. 193—194·4°, with 17% of 2-α-*hydroxy*-2′ : 2″-*dimethoxybenzhydryl*-1-*naphtholactone* (**IV**), m.p. 232·2—232·5°. The structure of (**II**) and (**III**) is proved by decarboxylation to o-*anisyl* 2- (62%), m.p. 74·5—76° (74·6—75·6°), and 1-*naphthyl ketone* (21%), m.p. 75—76° (76—76·5°), respectively, also obtained from 2- and 1-$C_{10}H_7{\cdot}CN$, respectively, by condensation with (**I**). The structure of (**IV**) is proved by synthesis from (**II**) and (**I**). Condensation of (**II**) and MgMeBr in boiling C_6H_6–Et_2O gives 78% of 2-α-*hydroxy-*α-o-*anisylethyl*-1-*naphtholactone*, m.p. 129·6—130·6°, reduced by Zn dust (Cu-activated) in NaOH–aq. EtOH to 2-α-o-*anisylethyl*-1-*naphthoic acid* (90%), m.p. 188·8—189·6°. Ring-closure by 90% H_2SO_4 and subsequent reduction by Zn–Cu–NaOH–H_2O then gives 5-*methoxy*-10-*methyl*-1 : 2-*benzanthracene* (**V**) (40%), m.p. 131—132·2° [*s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 204·6—205·2°; *picrate*, m.p. 187—188·4°], and a little 5-*methoxy*-10-*methyl*-1 : 2-*benz*-9-*anthrone* (**VI**), m.p. 158—159°. Me_2SO_4–KOH–EtOH converts (**VI**) into 5 : 9-*dimethoxy*-10-*methyl*-1 : 2-*benzanthracene*, m.p. 136·2—137·2° [*picrate*, m.p. 128·8—130°; *s*-$C_6H_3(NO_2)_3$ *compound*, m.p. 146·2—146·8°]. (**V**) is not carcinogenic. M.p. are corr.
R. S. C.

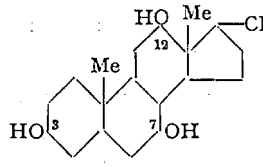
Synthetic experiments in the group of sympathomimetics. II. Poly- and hetero-cyclic ring systems. S. Rajagopalan (*Proc. Indian Acad. Sci.*, 1941, **13, A**, 566—572).—2 : 3 : 4 : 1-$NO_2{\cdot}C_6H_2(OMe)_2{\cdot}CHO$, 1-$C_{10}H_7{\cdot}CH_2{\cdot}CO_2K$, and Ac_2O at 105—110° (oil-bath) afford 2-*nitro*-3 : 4-*dimethoxy*-α-1′-*naphthylcinnamic acid*, m.p. 238—239° (decomp.), reduced by aq. NH_3–$FeSO_4$ to the 2-*NH*$_2$-compound, m.p. 201° (decomp.), which with *iso*-$C_5H_{11}{\cdot}O{\cdot}NO$ and conc. H_2SO_4 in (*iso*-$C_5H_{11})_2O$, followed by aq. NaH_2PO_2 (+ a little active Cu) at 40—50°, then at 80—90°, yields 11 : 12-*dimethoxychrysene*-7-*carboxylic acid*, m.p. 201—202° (decomp.), decarboxylated (Cu, quinoline) to 11 : 12-*dimethoxychrysene*, b.p. 210—220°/

1—2 mm. [*picrate*, m.p. 153—155° (decomp.)]. Glycerol, 3 : 1 : 2-NH_2·$C_6H_3(OMe)_2$ (**I**), conc. H_2SO_4, and $PhNO_2$ at 100° (bath), then at 130—135°, afford 7 : 8-*dimethoxyquinoline*, b.p. 148—150°/3—4 mm. [*picrate*, m.p. 182—184° (softens at 180°); *methiodide*, m.p. 182° (decomp.)]. (**I**), conc. HCl, $ZnCl_2$, and paraldehyde at 100°, then at 130—135°, give 7 : 8-*dimethoxy*-2-*methylquinoline*, b.p. 147—148°/2—3 mm. [*picrate*, m.p. 155—156° (decomp.); *methiodide*, m.p. 176—177° (decomp.)]. β-2 : 3-*Dimethoxyphenylethylacetamide*, m.p. 64—66°, and $POCl_3$–PhMe give 5 : 6-*dimethoxy*-1-*methyl*-3 : 4-*dihydro*isoquinoline, b.p. 141—143°/3 mm. [*hydrochloride*, m.p. 202—203° (decomp.); *picrate*, m.p. 214° (decomp.) (sinters at 210°); *methiodide*, m.p. 106—107° (decomp.)], reduced [Zn–aq. H_2SO_4 at 100° (bath)] to 5 : 6-dimethoxy-1-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, an oil [*hydrochloride*, m.p. 213—214° (decomp.); *picrate*, m.p. 196—198° (decomp.) (sinters at 194°)]. Aminoacetal (**II**), α-$C_{10}H_7$·OH, and AcOH–conc. HCl at room temp. afford *ββ-bis*-(4-*hydroxy*-1-*naphthyl*)*ethylamine hydrochloride*, m.p. 237—238° (decomp.). The product obtained from 1 : 2-$C_{10}H_6(OH)_2$ is unstable, and reaction does not occur using 8-hydroxyquinoline. (**II**), 3 : 4-dihydroxyphenanthrene, and AcOH–conc. HCl yield the unstable β-hydroxy-β-3 : 4-dihydroxy-*x*-phenanthrylethylamine (*picrate*, decomp. 195—197°). 3 : 4-Dimethoxyphenanthrene and hippuryl chloride in CS_2–HCl yield 3 : 4-*dimethoxy*-x-*phenanthryl benzamidomethyl ketone*, m.p. 268—269° (decomp.), in poor yield. A. T. P.

Preparation of a pregnane-3(α) : 17 : 20-triol. H. Hirschmann (*J. Biol. Chem.*, 1941, **140**, 797—806).—Pregnane-3(α) : 20(α)-diol and boiling AcOH give the 3-*acetate* (**I**), m.p. 131·5—132·5° (solvent-free specimen obtained only by sublimation in high vac.), the 20-acetate, new m.p. 175·5° (cf. Butenandt *et al.*, A., 1935, 215), and the diacetate, which are separated by chromatographic analysis. (**I**) and *p*-$C_6H_4Me·SO_2Cl$–C_5H_5N at room temp. yield *pregnanediol* 3-*acetate* 20-p-*toluenesulphonate*, m.p. 112—115° (decomp.), converted by $CaCO_3$–C_5H_5N, then aq. NaOH–MeOH, into Δ^{17}-*pregnen*-3(α)-*ol*, m.p. 118—120°, hydroxylated by OsO_4–Et_2O, then aq. Na_2SO_3–EtOH, to a *pregnane*-3(α) : 17 : 20-*triol* (**II**), m.p. 215—218°, purified through the *diacetate*, m.p. 193—196°, $[\alpha]_D^{20}$ +71° in EtOH (chromatographic separation), and hydrolysis with aq. NaOH–MeOH. (**II**) is not identical with 3(α) : 17 : 20-triol described by Butler *et al.* (A., 1938, II, 368); the difference is attributed to different spatial arrangement at $C_{(17)}$ or $C_{(20)}$ or both. (**II**) and aq. MeOH–H_2SO_4 give ætiocholan-3(α)-ol-17-one. M.p. are corr. A. T. P.

Toad bile. VII. Pentahydroxybufostane, $C_{25}H_{50}O_5$. T. Kazuno (*Z. physiol. Chem.*, 1940, **266**, 11—30; cf. A., 1937, II, 420).—The neutral portion of toad bile was fractionated by addition of NaCl (concn. 3%, 10%, and finally saturation). The first fraction gave a substance, m.p. 197°, yielding on hydrolysis 1 mol. of H_2SO_4 and cryst. *pentahydroxybufostane* (**I**), $C_{25}H_{50}O_5$, m.p. 172°, $[\alpha]_D^{24}$ +33·49° in EtOH. (**I**) is saturated (Br, $KMnO_4$, and H_2) and gives no ketone reaction. It therefore contains four rings (the *cyclo*pentanoperhydrophenanthrene nucleus). With AcOH–CrO_3 at 20°, (**I**) affords *dihydroxytriketobufostane* (**II**), m.p. 198·5—199° (*trioxime*, decomp. 234°), and *tetraketo*isobufostane (**III**), $C_{25}H_{42}O_4$, m.p. 245—248° (250°) (*tetraoxime*, m.p. 244°). (**II**) is reduced (H_2, PtO_2, AcOH) to (**I**), whilst (**III**) takes up 4 H_2 to yield *tetrahydroxy*isobufostane (**IV**), $C_{25}H_{50}O_4$, m.p. 204°. Incomplete hydrogenation (2 H_2) affords *dihydroxydiketo*isobufostane, m.p. 221—224°. (**IV**) shows a positive Hammarsten reaction indicating OH at positions 3, 7, and 12, yields no oxime or semicarbazone, and is converted by CrO_3 into (**III**). Similarly in dehydrocholic acid the CO at 3 and 7 are more easily hydrogenated than is that at $C_{(12)}$. Partial hydrolysis of the 3 : 7 : 12-*triacetate* (**V**), m.p. 117—119°, $[\alpha]_D^{24}$ +5·55° in MeOH, of (**I**) affords a *diacetate*, m.p. 165—166°, oxidised by CrO_3 to *dihydroxyketodiacetoxybufostane*, m.p. 149—150°, which is hydrolysed to *tetrahydroxy*-3-*ketobufostane*, m.p. 161° (*oxime*, m.p. 211°), giving a positive Jaffé reaction. (**III**) is probably formed from (**II**) by a pinacolic rearrangement; thus (**II**) can be rearranged to (**III**) by CrO_3 in AcOH. The same rearrangement occurs at 80—90° with (**V**), which yields (cf. below) (after hydrolysis) *trihydroxyketo*isobufostane (**VI**), m.p. 161°, isolated as the semicarbazone. CrO_3 converts (**VI**) into (**III**). The assumption that the side-chain contains a glycol group is confirmed by the conversion (cf. above) by CrO_3 of (**V**) into cholic acid triacetate, which was hydrolysed to cholic acid. By Clemmensen reduction, (**III**) gives iso-*bufostane* (**VII**), $C_{25}H_{50}$, m.p. 72°, and by partial reduction *triketo*isobufostane (**VIII**), m.p. 163°. (**VII**) is not identical with coprostane; it is probably 25-methylcoprostane. (**VIII**) shows no Jaffé reaction, indicating that the CO at $C_{(3)}$ is reduced. Thus the CO groups are at 7, 12, and 24.

The neutral *substance* (**IX**), $C_{24}H_{40}O_4$, m.p. 175°, $[\alpha]_D^{28}$ +30·27° in EtOH, from the fourth fraction occurs free in bile. With CrO_3 it gives a *triketone*, (**X**), $C_{24}H_{34}O_4$, m.p. 242°. It must thus belong to the cholane series and is named tetrahydroxycholane. As the Hammarsten reaction is positive and NaOH does not cause rearrangement of (**V**), 3 OH are at positions 3, 7, and 12. (**IX**) is thus regarded as an oxidation product of (**I**). The formation of the C_{24} bile acids from C_{27} and C_{28} sterols in the animal organism may proceed either by glycol oxidation coupled with ω-oxidation or by ω-oxidation together with β- or glycol oxidation. J. H. B.



(I.)

Synthesis of *dl*-"*o*"-thyronine. H. E. Ungnade (*J. Amer Chem. Soc.*, 1941, **63**, 2091—2093).—*p*-NO_2·C_6H_4·O·C_6H_4·OMe-*o* (prep. by Ullmann reaction; 64% yield) and H_2–Raney Ni at 100°/2000 lb. give *p*-NH_2·C_6H_4·O·C_6H_4·OMe-*o* (**I**) (86%), m.p. 96—97°, b.p. 149—150°/1 mm. [Ac derivative, m.p. 115—115·5° (lit. 118°)], converted (diazo-reaction) into the *p*-I-compound, b.p. 150—151°/2 mm., and thence (CuCN; 250°) *o*-*anisyl* p-*cyanophenyl ether* (**II**), m.p. 93—94°, b.p. 145—150°/1 mm., also obtained less well from (**I**) by a diazo-reaction. *o*-OMe·C_6H_4·OK, *p*-C_6H_4MeBr, and Cu powder at 150° give o-*anisyl* p-*tolyl ether*, m.p. 51·8—52·5°, converted by HI–AcOH–Ac_2O into 2-*hydroxy*-4′-*methyl*-, m.p. 63—63·8°, and by $KMnO_4$ in aq. C_5H_5N into 4′-*carboxy*-2-*methoxy*- (**III**), m.p. 159—160°, which with HI–AcOH gives 2-*hydroxy*-4′-*carboxy*-*diphenyl ether*, m.p. 139—139·5° [also obtained from (**II**) by HI–AcOH]. Stephen reduction of (**II**) gives only a trace of aldehyde [whence 2-*phenyl*-4-p-o′-*anisyloxybenzylidene*-5-*oxazolone* (**IV**), m.p. 184—185°]. *p*-OK·C_6H_4·CO_2Et, *o*-C_6H_4Br·OMe, and Cu powder at 240—260° give *o*-OMe·C_6H_4·O·C_6H_4·CO_2Et-*p*, b.p. 145—147°/1 mm. [with a little (**III**) and *o*-OMe·C_6H_4·OPh]. This yields p-o′-*anisyloxybenzhydrazide*, m.p. 130·5—131·5° [also prepared starting from (**III**)], the p-$C_6H_4Me·SO_2$ derivative, m.p. 205—206°, of which with Na_2CO_3 in $(CH_2·OH)_2$ at 160° (1·5 min.) gives p-o′-*anisyloxybenzaldehyde*, m.p. 56—56·5°, and thence (**IV**) and α-*amino*-β-p-o′-*hydroxyphenoxypropionic acid* [o-*thyronine*] (**V**), m.p. 240° (decomp.) (sinters at 238°; bath pre-heated to 200°). An impure I_2-derivative of (**V**) has no thyroid activity (tadpole), but di-iodotyrosine has some activity. Mixtures of "*p*"-thyronine and (**V**) can be analysed by means of the absorption spectra, which are given for both. R. S. C.

Synthesis of 3′ : 5′-difluoro-*dl*-thyronine and 3 : 5-di-iodo-3′ : 5′-difluoro-*dl*-thyronine. C. Niemann, A. A. Benson, and J. F. Mead (*J. Amer. Chem. Soc.*, 1941, **63**, 2204—2208).—Crude 4 : 3 : 1-OMe·$C_6H_3(NO_2)$·CO_2H (prep. from oil of anise by conc. HNO_3 and V_2O_5 first at 90° and then at the b.p.) and HCl–MeOH give the ester (86%), m.p. 108—109°, hydrogenated (PtO_2–MeOH) to 4 : 3 : 1-OMe·$C_6H_3(NH_2)$·CO_2Me (91%), m.p. 85—86°. Addition of HF–BF_3 to the derived diazonium chloride at −25° gives the diazonium fluoroborate (88%), decomposed by dry distillation at 50 mm. to *Me* 3-*fluoro*-4-*methoxybenzoate* (**I**) (56%), m.p. 70—71°, b.p. 116°/5 mm. With HNO_3 (*d* 1·5) at 0—5° this gives 4 : 3 : 5 : 1-OMe·$C_6H_2F(NO_2)$·CO_2Me (72%), m.p. 49·3—49·5°, hydrogenated (PtO_2–MeOH) to the NH_2-ester (92%), m.p. 51—54°, b.p. 117°/0·1 mm., which yields (diazo-reaction as above) *Me* 3 : 5-*difluoro*-4-*methoxybenzoate* (**II**) [30% and some (**I**)], m.p. 37·5°, b.p. 55°/0·2 mm. The derived (KOH–EtOH) acid (98%), m.p. 164—165°, with $SOCl_2$ and then NH_3–Et_2O gives the *amide* (91%), m.p. 158—160°, converted by NaOBr–NaOH at, successively, −10°, 25°, and 100° into 3 : 5-*difluoro*-p-*anisidine* (**III**) (77%), m.p. 78·5—79°, b.p. 80°/0·1 mm. (p-NO_2·C_6H_4·*CO* derivative, m.p. 207—207·5°). Nitration of *o*-C_6H_4F·OMe (**IV**) (prep. improved to give 64% yield) yields only 4 : 2 : 1-NO_2·C_6H_3F·OMe (cf. Holmes *et al.*, A., 1926, 831). With conc. H_2SO_4 at room temp. and then aq.

NaCl, (**IV**) gives *Na* 3-*fluoro*-4-*methoxybenzenesulphonate*, converted by HNO_3 (*d* 1·5) in H_2SO_4 at 0° followed by aq. NaCl into *Na* 3-*fluoro*-5-*nitro*-4-*methoxybenzenesulphonate* or, after keeping and then distillation in steam at 170°, into 2-*fluoro*-6-*nitrophenol* (37%), m.p. 90—91°. The Na salt thereof with Me_2SO_4 and PhMe at 110—120° gives 2-*fluoro*-6-*nitroanisole* (86%), m.p. 9°, b.p. 93°/3 mm., hydrogenated (PtO_2) to 2-*fluoro*-6-*aminoanisole* (84%), b.p. 94°/10 mm. (p-$NO_2{\cdot}C_6H_4{\cdot}CO$ derivative, m.p. 147—148·5°), which affords (diazo-reaction) 2 : 6-*difluoroanisole* (56%), b.p. 62°/40 mm. H_2SO_4–HNO_3 (*d* 1·5) then gives 2 : 6-*difluoro*-4-*nitroanisole* (88%), m.p. 37—38°, b.p. 71°/0·6 mm., hydrogenated (PtO_2–MeOH) to (**III**) (93%) (in some cases a little 3 : 5 : 3′ : 5′-*tetrafluoro*-4 : 4′-*dimethoxyazobenzene*, m.p. 163—164°, is also formed). Treatment of the diazonium sulphate from (**III**) with hot aq. $CuSO_4$ + xylene gives 3 : 5-*difluoro*-4-*methoxyphenol* (86%), m.p. 69—70°, b.p. 71°/0·2 mm., which with 3 : 4 : 5 : 1-$C_6H_2I_3{\cdot}NO_2$ and K_2CO_3 in boiling COMePr^a gives 2 : 6-*di-iodo*-3′ : 5′-*difluoro*-4-*nitro*-4′-*methoxydiphenyl ether* (73%), m.p. 127—128°, reduced by $SnCl_2$–AcOH to the amine (*hydrochloride*, m.p. 185—200°; *Ac* derivative, m.p. 219—220°). Treatment with *sec.*-BuO·NO in AcOH at 20—25° and then with aq. KCN–$CuSO_4$ at 90° gives 3 : 5-*di-iodo*-4-3′ : 5′-*difluoro*-4′-*methoxyphenoxybenzonitrile* (66%), m.p. 129—134°, converted by HI–AcOH into 3 : 5-*di-iodo*-4-3′ : 5′-*difluoro*-4′-*hydroxyphenoxybenzoic acid*, m.p. 232—234°, and by $SnCl_2$–HCl–Et_2O into 3 : 5-*di-iodo*-4-3′ : 5′-*difluoro*-4′-*methoxyphenoxybenzaldehyde* (72%), m.p. 124—126° [p-*nitrophenylhydrazone*, m.p. 280—281° (decomp.)], which yields 2-*phenyl*-4 -3′ : 5′-*di* - *iodo* - 4′-3″ : 5″-*difluoro*-4″-*methoxyphenoxybenzylidene*-5-*oxazolone*, sinters at 214·5°, m.p. 216—217°, and thence (Ac_2O–HI–red P) dl-3 : 5-*di-iodo*-3′ : 5′-*difluorothyronine* (60%), m.p. 248° (decomp.). This is converted by H_2–Pd–$CaCO_3$–NaOH into dl-3′ : 5′-*difluorothyronine*, m.p. 242—244°. 85% $N_2H_4{\cdot}H_2O$ and (**I**) give 3-*fluoro*-4-*methoxybenzhydrazide*, m.p. 178—179° (decomp.), the $PhSO_2$ derivative, m.p. 176—177°, of which with Na_2CO_3 in $(CH_2{\cdot}OH)_2$ at 155° gives crude 4 : 3 : 1-OMe·$C_6H_3F{\cdot}CHO$ (67%) and thence the azlactone, 3-*fluoro*-α-*benzamido*-4-*methoxycinnamic acid*, m.p. 221—222°, and *dl*-3-fluorotyrosine (12% over-all), decomp. 275—278° (rapid heating). (**II**) yields similarly 3 : 5-*difluoro*-4-*methoxybenzhydrazide*, m.p. 189—190° (decomp.) ($PhSO_2$ derivative, m.p. 179—180°), and thence as above *dl*-3 : 5-difluorotyrosine (13% over-all), decomp. 280° (rapid heating; lit. 265°). R. S. C.

Reduction of amines and substituted amides. II. Kinetics and mechanism of electro-reduction of amides. A. V. Koperina and M. M. Kliutschareva (*J. Gen. Chem. Russ.*, 1941, **11**, 51—62).—The chief product of reduction of NH_2Bz in aq. EtOH (Pb cathode, c.d. 0·024 amp. per sq. cm., at 10°) is $CH_2Ph{\cdot}NH_2$ (95%), with PhCHO and $CH_2Ph{\cdot}OH$ as by-products. The velocity of electro-reduction falls in the order $NH_2Br > NHBz{\cdot}CH_2{\cdot}CO_2H > NHMeBz > NMe_2Bz$. Reduction of $NHBz{\cdot}CH_2{\cdot}CO_2H$ in aq. EtOH involves production of $NHBz{\cdot}CH_2{\cdot}CO_2Et$, owing to which *N*-benzylglycine is not obtained in quant. yield. R. T.

Chemically marked antigens. II. Reactivity of oxazolones. H. Lettré and M. E. Fernholz (*Z. physiol. Chem.*, 1940, **266**, 37—40).—See A., 1941, III, 1078. The following esters of *dl*-benzoyl-α-alanine (**I**) have been prepared by heating 2-phenyl-4-methyloxazolone (**II**) with the appropriate alcohol: *Pr*$^\beta$, m.p. 79—80°, CH_2Ph, m.p. 88—89°, l-*menthyl*, m.p. 104—105°, *Ph*, m.p. 131—132°, β-$C_{10}H_7$, m.p. 164—165°, o-*carboxyphenyl*, m.p. 152—153°, and the *Ph thio*-ester (from PhSH), m.p. 130—131°. The *ethylamide*, m.p. 136—137°, *methylanilide*, m.p. 119—120°, and *piperidide*, m.p. 114—115°, of (**I**), and dl-*benzoylalanyl*-l-*proline*, m.p. 228—230°, have also been prepared. α-Terpineol, NH_2Bz, NHPhBz, and indole did not react with (**II**). J. H. B.

Relative directive powers of carboxyl and quaternary ammonium group. A. Zaki and W. Tadros (*J.C.S.*, 1941, 562—564).—*p*-$CHO{\cdot}C_6H_4{\cdot}NMe_3Cl$ with boiling fuming HNO_3, conc. HNO_3–H_2SO_4 at 100° (bath), or $KMnO_4$ yields (after suitable treatment) the following p-*carboxyphenyltrimethylammonium* salts: *picrate*, m.p. 207°; *iodide*, m.p. 238°; *perchlorate*, m.p. 284°; *chloride perbromide*, m.p. 200°; the *chloride* (**I**), m.p. 240—241°, with EtOH–NaOEt gives *p*-$NMe_2{\cdot}C_6H_4{\cdot}CO_2H$. Fuming HNO_3–conc. H_2SO_4 at 100° (bath) etc. converts (**I**) into the following 3-*nitro*-4-*carboxyphenyltrimethylammonium* salts: *picrate*, m.p. 198°; *iodide*, m.p. 236°; *perchlorate*, m.p. 259°; *chloride perbromide*, m.p. 158—159°; the *chloride*, m.p. 230—231°, with EtOH–NaOEt gives 2-*nitro*-4-*dimethylaminobenzoic acid*, m.p. 242° (darkens at 225°), decarboxylated to *m*-$NO_2{\cdot}C_6H_4{\cdot}NMe_2$. MeI could not be added to 3 : 4 : 1-$NO_2{\cdot}C_6H_3(NMe_2){\cdot}CO_2H$. A. Li.

Hydrogen bonds involving the C–H link. XV. Non-bonding of triphenylmethane hydrogen atoms. C. S. Marvel and J. Harkema (*J. Amer. Chem. Soc.*, 1941, **63**, 2221—2222).—*o*-, m.p. 84° (prep. from the acid by $SOCl_2$ at room temp. and removal of excess in N_2), and *p*-$CHPh_2{\cdot}C_6H_4{\cdot}COCl$ with $NHMe_2$ in Et_2O give o-, m.p. 146°, and p-*benzhydrylbenzdimethylamide*, m.p. 89—90°, respectively. Infra-red absorption spectra of the amides and corresponding Me esters (*p*-, new m.p. 78—79°) show max. only at 3·20 (aromatic C–H) and 3·32 μ. (aliphatic C–H), and the compounds are not associated (f.p.) in C_6H_6. H-bonding thus does not occur by chelation. R. S. C.

***n*-Amyl, m.p. 58°, *n*-hexyl, m.p. 52—53°, and *n*-octyl orsellinate, m.p. 61°.**—See A., 1941, III, 925.

Action of semicarbazide hydrochloride on β-*p*-anisylglutaconic anhydride. R. Y. Shahane (*Rasāyanam*, 1941, **1**, 222—223; cf. Limaye *et al.*, A., 1931, 1055).—The action of $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2$ on an aq. suspension of β-*p*-anisylglutaconic anhydride at 100° gives an additive *compound*, $C_{13}H_{15}O_5N_3$, which gives a colour with $FeCl_3$. The semicarbazone structure (Dixit, A., 1936, 847) cannot be accepted. H. W.

Constitution of tetrahydroxynorsterocholanic acid. H. Isaka (*Z. physiol. Chem.*, 1940, **266**, 117—122).—Tetrahydroxynorsterocholanic acid (**I**), $C_{27}H_{46}O_6$, is partly acetylated by AcCl–AcOH at room temp. to the *diacetate*, m.p. 230—231°, which is oxidised by CrO_3–AcOH to 12-*keto*-3 : 6-*diacetocholanic acid* (**II**), m.p. 210°. This is hydrolysed by KOH–EtOH to 3 : 6-*dihydroxy*-12-*ketocholanic acid*, $C_{24}H_{38}O_5$, m.p. 188—190°. By the same method iso*cholic acid diacetate*, m.p. 240°, affords (**II**). The semicarbazone of (**II**) by Wolff–Kishner reduction yields hyodeoxycholic acid. Thus the two *sec.*-OH of (**I**) and of *iso*cholic acid are at $C_{(3)}$ and $C_{(6)}$. On distillation in a high vac. (**I**) gives 12-*ketocholadienic acid*, $C_{24}H_{34}O_3$, m.p. 193—195°, reduced (H_2, Pd-black, AcOH) to 12-ketocholanic acid. This indicates another *sec.*-OH at $C_{(12)}$ in these acids. (**I**) is thus 3 : 6 : 12 : 24-tetrahydroxynorsterocholanic acid, confirming Ohta (A., 1939, II, 371). (**I**) gives the Hammarsten reaction, which is therefore positive not only with OH at $C_{(3)}$, $C_{(7)}$, and $C_{(12)}$, or $C_{(3)}$ and $C_{(12)}$ with double linking in ring B, but also with bile acids with OH at $C_{(3)}$, $C_{(6)}$, and $C_{(12)}$. J. H. B.

Action of hydrogen and Raney nickel on aromatic aldehydes. A. Albert and B. Ritchie (*J. Proc. Roy. Soc. N.S.Wales*, 1940, **74**, 373—376; cf. A., 1941, II, 39).—PhCHO is not reduced (H_2, Raney Ni; method, *loc. cit.*) at 25°, but at 70° yields 100% of $CH_2Ph{\cdot}OH$. *o*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ or *o*-$NH_2{\cdot}C_6H_4{\cdot}CHO$ is reduced (25°) to *o*-$NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$, *p*-$NO_2{\cdot}C_6H_4{\cdot}CHO$ (7 hr., 25°) to *p*-$NH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$, or (11 hr., 70°) to a mixture of *p*-$C_6H_4Me{\cdot}NH_2$ and poly-*p*-aminobenzyl alcohol, 2 : 4 : 1-$(NO_2)_2C_6H_3{\cdot}CHO$ (2 hr., 25°, coarse catalyst) to 2 : 2′-dinitro-4 : 4′-azoxytoluene (**I**), m.p. 165°, or (6 hr., 25°, coarse catalyst) to 2 : 1 : 4-$NO_2{\cdot}C_6H_3Me{\cdot}NH_2$, and (**I**) (8 hr., 50°) to 1 : 2 : 4-$C_6H_3Me(NH_2)_2$. A. Li.

Preparation of *o*-hydroxyaldehydes from phenols and hexamethylenetetramine. J. C. Duff (*J.C.S.*, 1941, 547—550; cf. A., 1934, 1213).—When heated at 150—155° with $(CH_2)_6N_4$ in glycerol previously heated at 170° with H_3BO_3, and the product hydrolysed (dil. H_2SO_4), PhOH, *o*-, *m*-, and *p*-cresol, *o*- and *p*-$C_6H_4Cl{\cdot}OH$, 2 : 4 : 1-$C_6H_3Cl_2{\cdot}OH$, 1 : 6 : 3-$C_6H_3MeCl{\cdot}OH$, *m*-5-xylenol, 1 : 3 : 2 : 5-$C_6H_2Me_2Cl{\cdot}OH$, *p*-$C_6H_4Ph{\cdot}OH$, β-$C_{10}H_7{\cdot}OH$, carvacrol, and thymol yield respectively (without isolable intermediate products) *o*-$OH{\cdot}C_6H_4{\cdot}CHO$, 2 : 1 : 3- [with 3 : 5-*dialdehydo*-*o*-*cresol*, m.p. 123° (*dioxime*, m.p. 199°)], 3 : 1 : 4-, and 4 : 1 : 3-$OH{\cdot}C_6H_3Me{\cdot}CHO$, 2 : 3 : 1- and 2 : 5 : 1-$OH{\cdot}C_6H_3Cl{\cdot}CHO$, 2 : 3 : 5 : 1-$OH{\cdot}C_6H_2Cl_2{\cdot}CHO$, 3 : 1 : 6 : 4-$OH{\cdot}C_6H_2MeCl{\cdot}CHO$ [with 6-*chloro*-2 : 4-*dialdehydo*-m-*cresol*, m.p. 113° (*dioxime*, m.p. 148°) (not obtained in the Reimer–Tiemann prep.)], 5 : 1 : 3 : 4-$OH{\cdot}C_6H_2Me_2{\cdot}CHO$, 2-*chloro*-4-*aldehydo*-m-5-*xylenol*, m.p. 96° (*oxime*, m.p. 197°) (also prepared by the Reimer–Tiemann method), 4 : 1 : 3-$OH{\cdot}C_6H_3Ph{\cdot}CHO$, 2 : 1-$OH{\cdot}C_{10}H_6{\cdot}CHO$ [better prepared in AcOH alone (*loc. cit.*)],

o-carvacrolaldehyde, b.p. 130°/15 mm. (*phenylhydrazone*, m.p. 150°), and *o*-thymolaldehyde, b.p. 130°/15 mm. (*oxime*, m.p. 123°). A possible intermediate is $CH_2Ar{\cdot}N{:}CH_2$, which isomerises to $CHAr{:}NMe$; hydrolysis then gives ArCHO and NH_2Me.
A. LI.

p-Bromophenacyl esters. D. T. Mowry and W. R. Brode (*J. Amer. Chem. Soc.*, 1941, **63**, 2281).—*Di*-p-*bromophenacyl oxalate*, m.p. 242° (decomp.), and p-*bromophenacyl Me succinate*, m.p. 104·6—104·8°, and *glutarate*, m.p. 46·6—46·8°, are described.
R. S. C.

Syntheses of 2-acylresorcinols by the "Nidhon" process. VII. Use of 7-hydroxycoumarin. D. B. Limaye and M. C. Joshi (*Rasāyanam*, 1941, **1**, 225—227).—Umbelliferone acetate is converted by anhyd. $AlCl_3$ at 160—165° into 8-*acetylumbelliferone* (**I**), m.p. 167° (*Me ether*, m.p. 126°; *semicarbazone*, m.p. 250°; *benzoate*, m.p. 145°), and 6-*acetylumbelliferone* (**II**), m.p. 177° (*semicarbazone*, m.p. >270°; *acetate*, m.p. 149°). (**I**) is hydrolysed by boiling N-NaOH to MeCHO, an *acid*, $C_{11}H_{10}O_5$, m.p. 184—210°, which loses CO_2 when heated above its m.p., and a very small proportion of 2 : 1 : 3-$C_6H_3Ac(OH)_2$ (**III**). (**II**) is very resistant towards NaOH, giving a very small yield of an acid, m.p. 220° (decomp.), but no (**III**). 7-Hydroxycoumarin (umbelliferone) can thus be used in the "Nidhon" process, but the method is not suitable for the prep. of (**III**) by reason of the small yield.
H. W.

Extension of the "Nidhon" process for the syntheses of 2-acylresorcinols to 2-acyl-4-alkylresorcinols. I. 2-Acetyl-4-ethylresorcinol. S. D. Limaye and D. B. Limaye (*Rasāyanam*, 1941, **1**, 201—207; cf. A., 1934, 298).—4 : 1 : 3-$C_6H_3Et(OH)_2$ (**I**), $CH_2Ac{\cdot}CO_2Et$, and conc. H_2SO_4 at room temp. give 4-methyl-6-ethylumbelliferone (**II**), m.p. 213° [*acetate* (**III**), m.p. 145°; *benzoate*, m.p. 155°; *Me ether*, m.p. 165°], hydrolysed by boiling 2N-NaOH to $COMe_2$ and (**I**). (**II**) is also obtained by reduction (Clemmensen) of 6-acetyl-4-methylumbelliferone. (**III**) and anhyd. $AlCl_3$ at 160° yield 8-*acetyl*-4-*methyl*-6-*ethylumbelliferone* (**IV**), m.p. 137° (*Me ether*, m.p. 95°; *semicarbazone*, m.p. >290°; *benzoate*, m.p. 139°), identified by reduction (Clemmensen) to 4-methyl-6 : 8-diethylumbelliferone, m.p. 137°, also obtained from 6-acetyl-4-methyl-8-ethylumbelliferone (**V**). (**IV**) is converted by boiling N-NaOH into $COMe_2$ and 2-acetyl-4-ethylresorcinol (**VI**), m.p. 130° (lit. 127°) (*Et*$_1$ *ether*, m.p. 84°), which with $CH_2Ac{\cdot}CO_2Et$ and $POCl_3$ affords (**V**). Reduction of (**VI**) by Zn–Hg and HCl affords 2 : 4 : 1'-3-$C_6H_2Et_2(OH)_2$, m.p. 96—97°.
H. W.

Condensation of β-arylglutaconic anhydrides with phenolic ethers. V. M. Bhave (*Rasāyanam*, 1941, **1**, 224).—*β-p*-Anisylglutaconic anhydride, PhOMe, and anhyd. $AlCl_3$ afford (probably) δ-keto-*β*δ-di-*p*-anisyl-Δ^{α}-pentenoic acid, m.p. 132° (decomp.), and its δ-enol-lactone, m.p. 174°.
H. W.

Naphthalene series. V. Properties of 2-stearyl-, -palmityl-, and -lauryl-1-naphthols and synthesis of 2-octadecyl-, -hexadecyl-, and -dodecyl-1-naphthols. R. D. Desai and W. S. Waravdekar (*Proc. Indian Acad. Sci.*, 1940, **12**, **A**, 507—512; cf. A., 1940, II, 252).—α-$C_{10}H_7{\cdot}OH$, stearic acid, and $ZnCl_2$ at 180° yield 2-*stearyl*-1-*naphthol* (**I**), m.p. 81—82° (*Me ether*, m.p. 42—43°; p-*nitrophenylhydrazone*, m.p. 89—90°), and some α-$C_{10}H_7$ *stearate*, m.p. 125° [with $AlCl_3$ at 140° gives (**I**)]. (**I**) and Br–AcOH at room temp., or HNO_3 (*d* 1·5)–AcOH, afford the 4-*Br*-, m.p. 84—85°, or 4-NO_2-compound, m.p. 71—72°, respectively. (**I**) is reduced (Clemmensen) to 2-*octadecyl*-1-*naphthol*, m.p. 119—120°. (**I**)–Ac_2O–NaOAc at 175—180° yield 2-*methyl*-3-*hexadecyl*-1 : 4-α-*naphthapyrone*, m.p. 73—74°, hydrolysed by 5% aq. NaOH (reflux) to (**I**). Similarly prepared are: 2-*palmityl*-1-*naphthol*, m.p. 83—84° (p-*nitrophenylhydrazone*, m.p. 94—95°; *Me ether*, m.p. 41—42°; 4-*Br*-, m.p. 86—87°, and 4-NO_2-derivative, m.p. 76—77°); 2-*hexadecyl*-1-*naphthol*, m.p. 124—125°; 2-*methyl*-3-*tetradecyl*-1 : 4-α-*naphthapyrone*, m.p. 89°; 2-*lauryl*-1-*naphthol*, m.p. 74—75° (p-*nitrophenylhydrazone*, m.p. 135—136°; *Me ether*, m.p. 37—38°; 4-*Br*-derivative, m.p. 65—66°); 2-dodecyl-1-naphthol, m.p. 150—151°.
A. T. P.

Synthesis of substances related to sterols. XXXVI (continuation of Part XXII). A. Koebner and (Sir) R. Robinson [with (in part) H. M. E. Cardwell]. **XXXVII. Derivatives of chrysene.** L. Golberg and (Sir) R. Robinson. **XXXVIII. Ethyl *cyclo*hexane-1 : 4-dione-2-carboxylate and other intermediates.** (Sir) R. Robinson and E. Seijo [with (in part) F. Litvan]. **XXXIX. (A) Derivatives of hydrindene. (B) Reduction of 1-γ-ketobutyl-2-naphthol.** F. J. McQuillin and (Sir) R. Robinson (*J.C.S.*, 1941, 566—575, 575—582, 582—586, 586—590).—XXXVI (cf. A., 1939, II, 75). 3-*β*-Naphthyl-*cyclo*pentanone-2-acetic acid (**I**) with $SnCl_4$ in CS_2 yields the isomeric *hydroxy-lactone*, m.p. 60° [*acetate* (Ac_2O containing HI, 15 min.), m.p. 157—158°, hydrolysed to (**I**)], which affords the semicarbazone of (**I**). Acetonyl-lævulic acid with 2% aq. KOH at 100° (bath) yields 3-*methyl*-Δ^2-cyclo*pentenone*-2-*acetic acid*, m.p. 109—110°. Difurfurylidene*cyclo*hexanone is hydrogenated (Pd–$SrCO_3$, EtOAc) to 2 : 6-*di*-α-*furyl*cyclo*hexanol*, b.p. 169°/2·5 mm., further reduced to a H_4-derivative, b.p. 180°/1 mm. *trans*-1-Ketodecahydronaphthalene with MgMeI in Et_2O–C_6H_6 yields trans-1-*methyldecahydro*-1-*naphthol*, b.p. 83—88°/2 mm., dehydrated (SO_2 in $COMe_2$) to 1-*methyloctahydronaphthalene*, b.p. 60°/0·4 mm., oxidised [$Pb(OAc)_4$, then AcOH–H_2SO_4] to a ketone. Methylation ($NaNH_2$ + MeI) of 3′ : 4-diketo-1 : 2 : 3 : 4-tetrahydro-1 : 2-*cyclo*pentenophenanthrene affords a *Me* derivative, m.p. 191—192°. $COPh{\cdot}CH_2Br$ with $COEt{\cdot}CHNa{\cdot}CO_2Et$ in Et_2O yields a product hydrolysed (aq. EtOH–NaOH) to 3-phenyl-2-methyl-Δ^2-*cyclo*pentenone, new m.p. 50—51° (2 : 4-*dinitrophenylhydrazone*, m.p. 232—233°) (with some $Bz{\cdot}[CH_2]_2{\cdot}CO_2H$), reduced ($H_2$, Pd–$SrCO_3$, EtOH) to the *-cyclo*pentanone, b.p. 112—114°/0·4 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 203—204°). Bromination of 2 : 6-$OMe{\cdot}C_{10}H_6{\cdot}COMe$ in $CHCl_3$ yields 5-*bromo*-6-*methoxy*-2-*naphthacyl bromide* (**II**), m.p. 134—135°, and some Br_3-derivative, m.p. 162—163°. (**II**) with excess of C_5H_5N at 100° gives the *pyridinium bromide*, m.p. 255—256° (decomp.), hydrolysed (NaOH) to 6 : 5 : 2-$OMe{\cdot}C_{10}H_5Br{\cdot}CO_2H$. (**II**) with $CHNaAc{\cdot}CO_2Et$ in Et_2O yields *Et* 5-*bromo*-6-*methoxy*-2-*naphthacylacetoacetate*, m.p. 78—80°, hydrolysed (aq. EtOH–NaOH) to 5-*bromo*-6-*methoxy*-2-*naphthacylacetone*, m.p. 176—177° (2 : 4-*dinitrophenylhydrazone*, m.p. ≮300°), which with NH_4OAc in AcOH gives a *pyrrole* derivative, $C_{18}H_{14}ONBr$, m.p. 173—175°. (**II**) with $COEt{\cdot}CHNa{\cdot}CO_2Et$ yields *Et* β-5-*bromo*-6-*methoxy*-2-*naphthacylpropionylacetate*, m.p. 89—91°, converted by hot aq. EtOH–NaOH into β-5-*bromo*-6-*methoxy*-2-*naphthoylpropionic acid*, m.p. 204—205°, and 3-(5′-*bromo*-6′-*methoxy*-2′-*naphthyl*)-2-*methyl*-Δ^2-cyclo*pentenone* (**III**), m.p. 177—178° [2 : 4-*dinitrophenylhydrazone*, m.p. 292—293° (decomp.)]. (**III**) and AcOH–HI (*d* 1·7) give 3-(6′-*hydroxy*-2′-*naphthyl*)-2-*methyl*-Δ^2-cyclo*pentenone*, m.p. 204—205°, whilst reduction (H_2, Pd–$SrCO_3$, EtOH, 60°) affords the *Me ether* (**IV**) (two forms), m.p. 116—117° and 84—86°, of 3-(6′-*hydroxy*-2′-*naphthyl*)-2-*methyl*cyclo*pentanone*, m.p. 143—144°. (**III**) with $(CH{\cdot}CO)_2O$ in boiling xylene yields (?) 8-*bromo*-3′-*keto*-7-*methoxy*-2-*methyltetrahydro*-1 : 2-cyclo*pentenophenanthrene*-3 : 4-*dicarboxylic anhydride*, m.p. 147—148°. 6 : 5 : 2-$OMe{\cdot}C_{10}H_5Cl{\cdot}COMe$ (modified prep.; cf. A., 1941, II, 295) with Br in $CHCl_3$ yields 5-*chloro*-6-*methoxy*-2-*naphthacyl bromide*, m.p. 116—117°, from which are obtained (as above) *Et* β-5-*chloro*-6-*methoxy*-2-*naphthacylpropionylacetate*, m.p. 87—89°, and 3-(5′-*chloro*-6′-*methoxy*-2′-*naphthyl*)-2-*methyl*-Δ^2-cyclo*pentenone*, m.p. 165—166° [2 : 4-*dinitrophenylhydrazone*, m.p. 296—297° (decomp.)] (with the naphthoylpropionic acid), reduced to the -cyclo*pentanone*, m.p. 137—139°, and (mainly) (**IV**), m.p. 84—86°. *x*-Norequilenin Me ether (**V**) is demethylated (HI) and acetylated to the *acetate*, m.p. 135—136° (picrate), a weak œstrogenic agent. Reduction (H_2, Pd–C + aq. $PdCl_2$, EtOH) of 3′ : 4-diketo- (**VI**) yields 3′-*keto*- (**VII**), m.p. 111—112° (2 : 4-*dinitrophenylhydrazone*, m.p. 255—256°), the 4′-*piperonylidene* derivative, m.p. 173—174°, of which is methylated (KOBu$^{\gamma}$–Bu$^{\gamma}$OH, MeI) to 3′-*keto*-4′-*piperonylidene*-2-*methyl*-, m.p. 158—159°, -1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene*. The 16-*piperonylidene* derivative, m.p. 187—188°, of (**V**) is similarly methylated to 16-*piperonylidene*-x-*equilenin Me ether* [3′-*keto*-7-*methoxy*-4′-*piperonylidene*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene*], m.p. 180—181°, which, like the stereoisomeric 16-*piperonylidene*-*equilenin Me ether*, m.p. 208—209°, cannot be further methylated. 1-*Keto*-6-*methoxy*-2-*piperonylidene*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 171—172°, is not methylated by MeI in Bu$^{\gamma}$OH–KOBu$^{\gamma}$, which converts 5-*methoxy*-2-*piperonylidene*-α-*hydrindone*, m.p. 226—227°, into an *isomeride* (or dimeride), m.p. 253—254°. (**VI**) with boiling $PhNO_2$–EtOH–aq. NaOH followed by Ac_2O yields 3′-keto-4-acetoxy-1 : 2-*cyclo*pentenophenanthrene. (**V**) when boiled with PhCHO–EtOH–aq. NaOH and then exposed to air yields 3′-*keto*-7-*methoxy*-4′-*benzylidene*-1 : 2-cyclo*pentenophenanthrene* (also $+0{\cdot}5H_2O$), m.p. 224°. 3′-Keto-4 : 7-dimethoxy- is partly

reduced (H_2, PtO_2, aq. $FeCl_3$, AcOH) to 4 : 7-*dimethoxy*-1 : 2-cyclo*pentenophenanthrene*, m.p. 119—122° (shrinking at 114°). The *oxime*, m.p. 244—246° (*acetate*, m.p. 209—210°), of 3′-keto-7-methoxy-4-ethoxy-1 : 2-*cyclo*pentenophenanthrene is partly reduced (H_2, PtO_2, Ac_2O) to the 3′-*acetamido*-compound, m.p. 219—221°, which could not be hydrolysed to the base. Hydrolysis and re-esterification of Me (*cis*-)3-6′-methoxy-2′-naphthyl*cyclo*pentanone-2-acetate (**VIII**), m.p. 61° (A., 1939, II, 75) gives probably the trans-*isomeride*, m.p. 101—102°. The *trans*-acid, m.p. 147°, when hydrogenated in AcOH yields a gummy acid which reverts to the original when heated with aq. NaOH and acidified; both acids on cyclisation give the same result. Methylation (Bu$^{\gamma}$OH–KOBu$^{\gamma}$–MeI) and hydrolysis of (**VIII**) yields 3-6′-*methoxy*-2′-*naphthyl*-2 : 5 : 5-*trimethyl*cyclo*pentanone*-2-*acetic acid*, m.p. 193—195°. (**VII**) with MgMeI yields 3′-*hydroxy*-3′-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2-cyclo*pentenophenanthrene*, m.p. 112—113°.

XXXVII (cf. A., 1933, 828). *Et* 4 : 4′-*dimethoxydesylacetate*, b.p. 220—225°/0·14 mm. (from deoxyanisoin, $CH_2Br{\cdot}CO_2Et$, and EtOH–NaOEt) (free *acid*, m.p. 110°), with $CH_2Br{\cdot}CO_2Et$ and Zn in C_6H_6 yields *β-hydroxy-βγ-dianisyladipolactone*, m.p. 186° (decomp.). δε-Dianisyl-βη-dimethylloctane-βη-diol-*a* (Dodds *et al.*, A., 1939, II, 312) with AcOH–HI at 150° yields 5 : 14-*dimethoxy*-2 : 2 : 11 : 11-*tetramethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-a, m.p. 219° (which yields no picric acid when boiled with AcOH–HNO_3), dehydrogenated (Se) to 5 : 14-*dimethoxy*-2 : 11-*dimethylchrysene*, m.p. 199° [*picrate*, m.p. 190° (sinters 169—171°)], also obtained from 2 : 11-diketo-5 : 14-dimethoxy-1 : 2 : 9 : 10 : 11 : 18-hexahydrochrysene-*a* and MgMeI. $(CO_2Me{\cdot}CH_2{\cdot}CHPh)_2$-*a* (*meso*) with MgMeI yields δε-*diphenyl*-βη-*dimethyloctane*-βη-*diol*-a, m.p. 125°, cyclised (AcOH–HI at 90°) to 2 : 2 : 11 : 11-*tetramethyl*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*-a, m.p. 173°, dehydrogenated (Se) to 2 : 11-dimethylchrysene. δε-*Dianisyl*-βη-*dimethyloctane*-βη-*diol*-b (prepared as above), m.p. 120°, could not be cyclised. 4 : 3′ : 4′-Trimethoxychalkone, m.p. 80° (lit. 80—81°; 90°; 137—138°) [from 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}COMe$, *p*-$OMe{\cdot}C_6H_4{\cdot}CHO$, and NaOH in aq. EtOH] with MeOH–NaCN yields γ-*keto*-α-*cyano*-α-*anisyl*-γ-3 : 4-*dimethoxyphenylpropane*, m.p. 112—114°, hydrolysed (AcOH–conc. H_2SO_4) to *β-veratroyl*-α-*anisylpropionamide*, m.p. 174—175°, and thence (aq. EtOH–NaOH) to the *acid*, m.p. 184—185°, reduced (Clemmensen) to α-*anisyl*-γ-3 : 4-*dimethoxyphenylbutyric acid*, m.p. 77—79° (*Me* ester, b.p. 220—222°/1 mm., m.p. 41—43°). This with boiling $POCl_3$ affords 1-*keto*-6 : 7-*dimethoxy*-2-*anisyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (**IX**), m.p. 141—142° (p-*nitrophenylhydrazone*, m.p. 205—207°), reduced (Na + PrOH) to 1-*hydroxy*-6 : 7-*dimethoxy*-2-*anisyl*-1 : 2 : 3 : 4-*tetrahydro*-, b.p. 214—215°/0·23 mm., dehydrated (PBr_3 in Et_2O) to 6 : 7-*dimethoxy*-2-*anisyl*-3 : 4-*dihydro-naphthalene*, m.p. 155—156°. (**IX**) with $CH_2{:}CH{\cdot}CH_2{\cdot}MgBr$ in Et_2O–C_6H_6 gives 6 : 7-*dimethoxy*-2-*anisyl*-1-*allyl*-3 : 4-*dihydronaphthalene*, b.p. 207—210°/0·5 mm., and with $CH_2Br{\cdot}CO_2Et$ and Zn in C_6H_6 affords (after hydrolysis with aq. EtOH–KOH) a mixture of γ-(1-*hydroxy*-6 : 7-*dimethoxy*-2-*anisyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*naphthyl*)*acetoacetic acid lactone* (**X**), m.p. 237—238° (*Me ether*, m.p. 209—210°; p-*nitrophenylhydrazone*, m.p. 203—205°), and 6 : 7-*dimethoxy*-2-*anisyl*-3 : 4-*dihydro*-1-*naphthylacetic acid*, m.p. 169—171° (which gives no turbidity with Br in aq. Na_2CO_3), hydrogenated (Pd–$SrCO_3$, EtOH) to the 1 : 2 : 3 : 4-*tetrahydro-acid*, m.p. 192—194° (with a small amount of an acid, m.p. 180—183°). This is cyclised (P_2O_5 in C_6H_6) to 2-*keto*-5 : 14 : 15-*trimethoxy*-1 : 2 : 9 : 10 : 11 : 18-*hexahydrochrysene*, m.p. 166—168° (*semicarbazone*, m.p. 220°), reduced (Clemmensen) to a saturated (non-homogeneous) *substance*, m.p. 193°. (**X**) is sol. in alkali and repptd. on acidification, and when heated at 250° yields 6 : 7-*dimethoxy*-2-*anisyl*-1-*acetonylidene*-, m.p. 214—215° (2 : 4-*dinitrophenylhydrazone*, m.p. 228—230°), hydrogenated (Pd–$SrCO_3$, EtOH) to -1-*acetonyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 142—145°. 3 : 4 : 3′-*Trimethoxychalkone*, m.p. 66—68° [from *m*-$OMe{\cdot}C_6H_4{\cdot}COMe$, 3 : 4 : 1-$(OMe)_2C_6H_3{\cdot}CHO$, and aq. EtOH–NaOH], yields (as above) *β*-m-*anisoyl*-α-3 : 4-*dimethoxyphenyl-propionitrile*, m.p. 98—99°, and -*propionamide*, m.p. 177—178°, γ-m-*anisyl*-α-3 : 4-*dimethoxyphenylbutyric acid*, m.p. 78° (*Me* ester, m.p. 64—65°), and 1-*keto*-6 : 3′ : 4′-*trimethoxy*-2-*phenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 145—146°.

XXXVIII. The keto-acetal from $CO(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$, $CH(OEt)_3$, and AcCl with NaOEt in Et_2O, then dil. HCl, yields *Et* cyclo*hexane*-1 : 4-*dione*-2-*carboxylate* (**XI**), b.p. 116—120°/0·5 mm., which with $Ph{\cdot}[CH_2]_2{\cdot}Br$ and EtOH–KOEt gives a *β-phenylethyl* derivative, b.p. 175—185°/0·7 mm., hydrolysed to the *acid*, m.p. 129—130° (*Me* ester 2 : 4-*dinitrophenylhydrazone*, m.p. 113—114°). (**XI**) is hydrolysed (H_2O at 190° under pressure) to *cyclo*hexane-1 : 4-dione. $CO(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$ with paraformaldehyde and ~20% aq. HCl yields after esterification (EtOH–H_2SO_4) *β*-(*β′-carbethoxypropionyl*)*butyrolactone*, b.p. 179—183°/0·5 mm. (*semicarbazone*, m.p. 171—173°; 2 : 4-*dinitrophenylhydrazone*, m.p. 148—152°), which when treated with $CH_2Ac{\cdot}CO_2Et$ (NaOEt), hydrolysed (conc. HCl), and re-esterified yields *Et* 4-*carbethoxy*-3-*methyl*-Δ^2-cyclo*hexenone*-2 : 6-*diacetate*, b.p. 189—191°/0·15 mm., with *substances*, b.p. 150—151°/0·2 mm., 155—156°/0·2 mm., and 161—163°/0·2 mm. $CO(CH_2{\cdot}CH_2{\cdot}CO_2H)_2$ is reduced (Na–Hg + H_2O) to *β*-(*β′*-carboxyethyl)butyrolactone. *cyclo*Hexanone (**XII**) and $CH_2(CH_2{\cdot}CO_2Me)_2$ with Na in C_6H_6 at successively 0°, room temp., and the b.p. yield *Me* δ : 2-*diketo*-δ-cyclo*hexylvalerate*, b.p. 132—143°/0·2 mm. (? *bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 247°), which with cold conc. H_2SO_4 gives the *enol lactone*, b.p. 120—123°/0·1 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 189°), of δ : 2-diketo-δ-*cyclo*hexylvaleric acid. (**XII**) and $(CH_2{\cdot}CO_2Me)_2$ with MeOH–NaOMe at 0° yield *Me pentamethyleneparaconate*, m.p. 73·5—74·5° (no colour with $FeCl_3$); the distilled product, b.p. 145°/0·5 mm. (colour with $FeCl_3$), in EtOH + aq. $FeCl_3$ (1 drop) affords ? *Me H* cyclo*hexylidenesuccinate*, m.p. 99—101°, and is hydrolysed (aq. NaOH or cold conc. HCl) to cyclo*hexylidenesuccinic acid*, m.p. 186—187°; these three substances are oxidised ($KMnO_4$) to (**XII**). $CMeNaAc{\cdot}CO_2Me$ with $CO_2Me{\cdot}[CH_2]_2{\cdot}COCl$ in Et_2O yields Me *β*-keto-α-acetyl-α-metbyladipate, hydrolysed (anhyd. NH_3 in Et_2O) to Me *β*-keto-α-methyladipate, which when treated with $COMe{\cdot}[CH_2]_2{\cdot}NMe_3I$ and NaOMe in C_5H_5N yields (2 hr. at 0°, 2 hr. at 100°) 3-*β-carbomethoxyethyl*-4-*carbomethoxy*-4-*methyl*-, b.p. 164°/0·3 mm., or (2 hr. at 0°, 8 hr. at the b.p.) 3-*β-carboxyethyl*-4-*methyl*-Δ^2-cyclo*hexenone*, m.p. 80—83°.

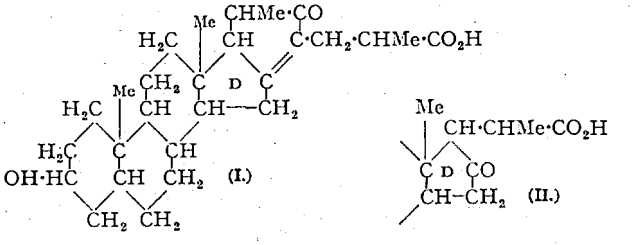
XXXIX (cf. A., 1938, II, 411). Hydrindene, $(CH_2{\cdot}CO)_2O$, and $AlCl_3$ in $PhNO_2$ yield γ-*keto*-γ-5-*hydrindylbutyric acid*, m.p. 123°, oxidised (NaOCl) to hydrindene-5-carboxylic acid, and reduced (Clemmensen) to γ-5-*hydrindylbutyric acid*, m.p. 48°, which is cyclised (H_2SO_4) to 8-*keto*-5 : 6 : 7 : 8-*tetrahydro*-2 : 3-cyclo*pentenonaphthalene* (**XIII**), b.p. 128—130°/0·2 mm. The *semicarbazone*, m.p. 245°, of (**XIII**) when heated with solid KOH at 20 mm. and the product dehydrogenated (Pd–C at 300°) yields 5 : 6-*benzhydrindene*, m.p. 94° (*picrate*, m.p. 118°). (**XIII**) with MgMeI followed by dehydrogenation yields 3′-*methyl*-5 : 6-*benzhydrindene*, b.p. 170—172°/20 mm. (*picrate*, m.p. 109—110°). Hydrindan-5-one with $NaNH_2$ in Et_2O followed by $COEt{\cdot}[CH_2]_2{\cdot}NMeEt_2I$ in C_5H_5N yields 6-*keto*-5-*methyl*-7 : 8-*dihydro*-1 : 2(or 2 : 3-)cyclo*pentenonaphthalene*, b.p. 153—155°/1·6 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 174—175°), which when dehydrogenated (Se) gives a *phenol*, $C_{14}H_{14}O$, m.p. 162—163°, and when reduced (H_2, Pd, EtOH, then Clemmensen) and dehydrogenated gives a substance, m.p. 38—42° (? 3′-methyl-4 : 5-benzhydrindene, *loc. cit.*). *β*-$C_{10}H_7{\cdot}OH$ with $COMe{\cdot}[CH_2]_2{\cdot}Cl$ in EtOH–KOEt at 0° yields 1-γ-ketobutyl-2-naphthol (**XIV**) (*semicarbazone*, m.p. 179—180°). This, its *oxime*, m.p. 168—169°, or *acetate*, b.p. 174—176°/0·2 mm., is reduced (H_2, PtO_2, AcOH) to a *methyltetrahydrobenzchroman*, m.p. 69°, dehydrogenated (Pd–C) to 2-*methyl*-5 : 6-*benzchroman*, m.p. 90—91°. $Al(OPr^{\beta})_3$–$Pr^{\beta}OH$ reduces (**XIV**) to 1-γ-*hydroxybutyl*-2-*naphthol*, m.p. 135—136°, which is reduced (H_2, PtO_2, AcOH, 60°) to some *methyldecahydrobenzchroman*, b.p. 123—126°/0·5 mm. Et *cyclo*hexanone-2-carboxylate in EtOH–NaOEt yields with $COEt{\cdot}[CH_2]_2{\cdot}NEt_2$, *Et* 3-*keto*-4-*methyl*-$\Delta^{4:10}$-*octahydronaphthalene*-9-*carboxylate*, b.p. 135—136°/0·2 mm. (*semicarbazone*, m.p. 166—167°), and with $COMe{\cdot}[CH_2]_2{\cdot}NEt_2$, *Et* 2-γ-*ketobutyl*cyclo*hexanone*-2-*carboxylate*, b.p. 176—180°/12 mm., which with Mg and a trace of I in Et_2O–C_6H_6 gives Et 4-keto-$\Delta^{5:10}$-octahydronaphthalene-9-carboxylate, with no pinacol. A. LI.

Preparation of dibenzpyrenequinone. II. Structure of isomeride of benzoylbenzanthrone. N. K. Moschtschinskaja (*J. Gen. Chem. Russ.*, 1941, **11**, 45—50; cf. A., 1939, **II**, 555). —2-Benzoylbenzanthrone (prep. Schaarschmidt, A., 1917, i, 274) has m.p. 237·8° (lit. 206°). The chief product of condensation of BzCl with benzanthrone in presence of $AlCl_3$ is 3-benzoylbenzanthrone, with 9-*benzoylbenzanthrone*, m.p. 206·2°, as a by-product. This is oxidised by CrO_3 in AcOH to 6-*benzoylanthraquinone*-1-*carboxylic acid*, m.p. 349°. R. T.

16-Hydroxymethylenecestrone.—See B., 1941, III, 296.

Conjugation of œstrogens with proteins. I. L. F. King and W. R. Franks (*J. Amer. Chem. Soc.*, 1941, **63**, 2042—2045).—The K salt of œstrone [2 : 4-*dinitrophenylhydrazone*, m.p. 278—280° (decomp.) (darkens at 268°)] with, best, *p*-$C_6H_4F{\cdot}NO_2$ and Cu dust at 200—210° gives *œstrone p-*$NO_2{\cdot}C_6H_4$ *ether* (65%), m.p. 192—194°, reduced ($SnCl_2$) to the p-$NH_2{\cdot}C_6H_4$ *ether* (**I**), m.p. 166·5—168·5° [*picrate*, m.p. ~160° (decomp.) (darkens at 120°); *semicarbazone*, m.p. ~295°; 2 : 4-*dinitrophenylhydrazone*, m.p. 238—240° (decomp.); N-*Ac* derivative ($+xH_2O$), softens at 100° and 170°, resolidifies, m.p. 201—202°, or (anhyd.) softens at 170—172°, resolidifies, m.p. 202—204°]. The product, m.p. 138—143°, from (**I**) and $COCl_2$ in C_6H_6–PhMe with boiling MeOH and EtOH gives the corresponding *Me*, m.p. 210—212° (softens at 207°), and *Et carbamate*, m.p. 163—165° (softens at 160°), respectively. Diazotisation of (**I**) and coupling with casein at p_H 8—10 then gives an orange-yellow conjugated azoprotein (**II**). The œstrogenic activity of (**I**) is fairly high and 10 times that of (**II**). *Ph* p-*aminobenzyl ether*, m.p. 71—73° (vac.) (*picrate*, m.p. 80·5—82·5°), is obtained by reducing ($SnCl_2$, AcOH–HCl) the NO_2-ether at 0°, but is unstable; conjugation with casein gives an azoprotein, which cannot be extracted by cold org. solvents. *Œstrone* p-*nitrobenzyl ether*, m.p. 176·5—178·5° (semicarbazone, m.p. 273—275°), and 4 : 4′-*di*-p-*nitrobenzyloxy-αβ-diethylstilbene*, m.p. 183—185°, are prepared but cannot be reduced to amines. Coupling of *p*-$NO_2{\cdot}C_6H_4{\cdot}N_2Cl$ with œstrogens failed. Micro-Kjeldahl analysis of the œstrone derivatives is modified to give correct results. R. S. C.

Sterols. CXXII. Sapogenins. LXIX. Structure of the side-chain of sarsasapogenin. Anhydrosarsasapogenoic acid. R. E. Marker, A. C. Shabica, and D. L. Turner (*J. Amer. Chem. Soc.*, 1941, **63**, 2274—2275; cf. A., 1941, II, 199, 257).—Anhydrosarsasapogenoic acid is (**I**) (cf. Fieser *et al.*, A., 1939,



II, 31, 437), since with O_3 in $CHCl_3$ at 0° it gives 3(*β*)-*hydroxy*-16-*ketobisnorcholanic acid* (**II**), m.p. 285° (decomp.), reduced by Na–EtOH to sarsasapogeninlactone. R. S. C.

Antihæmorrhagic activity of sulphonated derivatives of 2-methylnaphthalene. M. B. Moore (*J. Amer. Chem. Soc.*, 1941, **63**, 2049—2051).—The following relative antihæmorrhagic activities are reported, the salts being sol. in H_2O. 1 : 2 : 4-O:$C_{10}H_5Me$:O (**I**), Na (**II**), or $CH_2Ph{\cdot}NH_3$ (**III**) 1 : 4-dihydroxy-2-methylnaphthalene-3-sulphonate 100, 3-*β*-dimethylaminoethylamino-2-methyl-1 : 4-naphthaquinone hydrochloride ~25 (free *base*, a glass, prepared from 2-methyl-1 : 4-naphthaquinone 2 : 3-oxide and $NMe_2{\cdot}[CH_2]_2{\cdot}NH_2$ in abs. EtOH at room temp.), *K* 2-*methyl*-1 : 4-*naphthaquinone*-3-*sulphonate* (**IV**) 1·25, 2 : 1- 0·0013, 2 : 6- and 2 : 8-$C_{10}H_6Me{\cdot}SO_3Na$ 0, 2 : 1-$C_{10}H_6Me{\cdot}NO_2$ (m.p. 81—82°) 0·0016, and 1-*amino*-2-*methylnaphthalene*-4-*sulphonic acid* 0·002. (**II**), (**III**), and similar salts are obtained (but could not be isolated in a cryst. condition) from (**I**) and the appropriate $RHSO_3$ in H_2O or EtOH; the K salt is oxidised to (**IV**). R. S. C.

Dynamics of oxidation of alkyl-substituted organic compounds by chromic acid. I. Oxidation of 2-methylanthraquinone and its 1-nitro- and 1-chloro-derivatives to anthraquinone-2-carboxylic acids. M. A. Iljinski and V. A. Kazakova (*J. Gen. Chem. Russ.*, 1941, **11**, 16—22).—The velocity of oxidation of 2-methylanthraquinone (**I**) or its 1-NO_2- (**II**) or 1-Cl-derivative (**III**) (CrO_3 in AcOH at 70°) falls rapidly with rising [H_2O] of the systems, being practically nil in 80% AcOH. The velocity of oxidation of (**I**) is considerably > of (**II**). Both (**III**) and 1-chloroanthraquinone-2-carboxylic acid undergo profound decomp. under the reaction conditions. Directions for the prep. of anthraquinone-2-carboxylic acid and its 1-NO_2- and 1-Cl-derivative, in 98, 88, and 87% yield, respectively, are given. R. T.

III.—TERPENES.

Mutarotation of ethyl-alcoholic solutions of *l*-menthyl benzoylformate. M. M. Jamison and E. E. Turner (*J.C.S.*, 1941, 538—542).—In anhyd. EtOH at 18·8°, the mutarotation of *l*-menthyl benzoylformate is too rapid to be measured, $[\alpha]^{18\cdot8}_{5461}$ being −60·8° (unaffected by addition of traces of H_2O), but at 0° is measurable, follows a first-order law, and gives final $[\alpha]^{0}_{5461}$ −64° to −65°. The mutarotation observed by McKenzie *et al.* (A., 1929, 877) was due to the (unsuspected) presence of traces of H_2O in their abs. EtOH. It is suggested that mutarotation is caused by hemiacetal formation, an ionic mechanism occurring in presence of traces of H_2O. A. Li.

Bornyl chloride and its isomerides. G. A. Rudakov and I. G. Eroschevski (*J. Gen. Chem. Russ.*, 1940, **10**, 1958—1960).—The hydrocarbon, b.p. 157·8—158·5°, obtained by Liubomilov *et al.* (A., 1940, II, 228) by elimination of HCl from the liquid fraction of the additive product from pinene and HCl, is identified as *α*-fenchene. R. T.

Dehydrogenation of borneol in the vapour phase, using activated nickel catalyst. B. N. Rutovski and P. A. Muliar (*J. Appl. Chem. Russ.*, 1941, **14**, 173—180).—Camphor is obtained in 62—88% yield by passing borneol vapour over Raney Ni activated with alkali or alkaline-earth oxides, at 350°; the activating action of these oxides rises with increasing at. wt. of the metals. The activity of $CuCO_3$ at 350° is very considerably raised by adding 0·25% of KOH. R. T.

***p*-Aminobenzenesulphonamide camphorate.**—See B., 1941, III, 296.

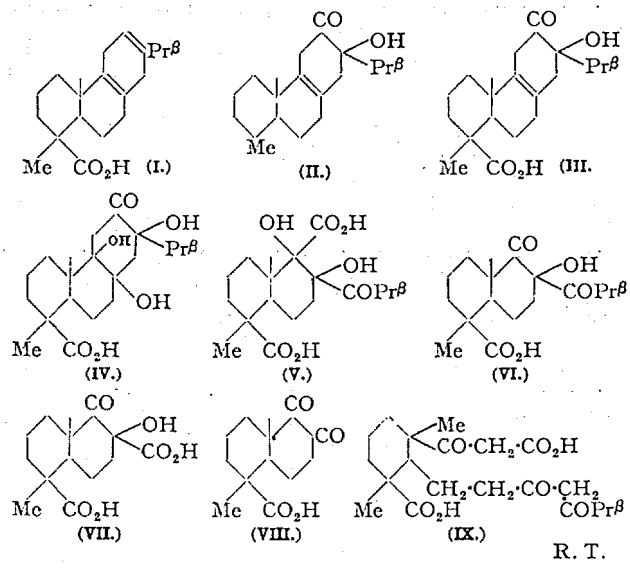
Sesquiterpenes from *Lansium annamalayanum*.—See B., 1941, III, 268.

Sapogenins. XI. Constitution of quillaic and oleanolic acids. P. Bilham and G. A. R. Kon (*J.C.S.*, 1941, 552—561).—Deoxyquillaic (**I**) and echinocystic acid (**II**) are identical [comparison of the acids and various derived CO-compounds (cf. White *et al.*, A., 1939, II, 333)]. (**I**) or (**II**) with 50% AcOH–HBr and Ac_2O at room temp. yields the same iso*diacetyl-lactone*, m.p. 275°. Quillaic acid diacetyl-lactone (A., 1939, II, 436) or its *semicarbazone*, m.p. 256—258°, is reduced (N_2H_4,H_2O and EtOH–NaOEt at 200° under pressure) to the *lactone*, m.p. 272° (*Ac*$_2$ derivative, m.p. 282—283°), of (**I**). Hydrogenation (PtO_2, AcOH) of the *trans*-monoketone previously described (A., 1941, II, 19) yields *α-norechinocystenol*, m.p. 210—211°, $[\alpha]_D$ −26·5° in $CHCl_3$ (acetate, m.p. 170—171°); the *β*-form (*loc. cit.*) has $[\alpha]_D$ −23° in $CHCl_3$. *trans*-Norhederabetulene, new m.p. 157°, when boiled with Zn–Hg in AcOH–HCl yields *norhederabetulene-III*, m.p. 166—167°, $[\alpha]_D$ +31·4° in $CHCl_3$. Me oleanonate is reduced (N_2H_4,H_2O and NaOEt under pressure) to pure *γ*-oleananic acid, or (Zn–Hg in AcOH–HCl) to the Me ester, m.p. 170—172°, of *β-oleananic acid* ($+H_2O$), m.p. 234°. Both acids on heating yield oleanene-II. Measurements on unimol. films of these acids, hedraganic acid, and their esters suggest that the CO_2H group is attached to one of the end rings, probably to $C_{(20)}$; $OH^{(2)}$ would then be on $C_{(10)}$. A possible new formulation for sapogenins of the *β*-amyrin group is discussed. A. Li.

Saponins and sapogenins. XIX. Decarboxylation of echinocystic acid. C. R. Noller and J. F. Carson (*J. Amer. Chem. Soc.*, 1941, **63**, 2238—2239).—At 280° (later 300—320°)/~10 mm. echinocystic acid (**I**) gives by loss of CO_2 and H_2O *norechinocystadienol* (**II**), m.p. 192—195°, $[\alpha]^{24}_D$ +81·8° in dioxan (*benzoate*, shrinks at 230°, m.p. 231—233°), which contains two conjugated ethylenic linkings in adjacent rings (absorption max. at 2410 A.) and does not react with (:CH·CO)$_2$O, H_2–catalyst, or Na–BuOH. Distillation of the monoacetate of (**I**) in a vac. and hydrolysis of the resulting product also gives (**II**). Structures are suggested for (**I**) and (**II**). R. S. C.

Resinic acids of conifers. V. Structure of *γ*-sapinic acid. V. N. Krestinski, E. V. Kazeeva, and N. F. Komschilov (*J. Appl. Chem. Russ.*, 1941, **14**, 229—238).—The following products were obtained by oxidation ($KMnO_4$ in 1% NaOH) of *α*-sapinic acid (**I**): a ketone (**II**), $C_{19}H_{30}O_2$, and the acids $Pr^{\beta}CO_2H$, $C_{20}H_{30}O_4$ (**III**), m.p. 201—204°; $C_{20}H_{32}O_6$ (**IV**), m.p. 131—134°, $C_{20}H_{32}O_7$ (**V**), $C_{18}H_{28}O_5$ (**VI**), $C_{14}H_{20}O_6$ (**VII**), and $C_{13}H_{18}O_4$ (**VIII**). With O_3 (**I**) yields a diozonide, which

decomposes at 100° to the acid $C_{20}H_{30}O_7$ (**IX**). The following structures are assigned :



R. T.

IV.—MISCELLANEOUS UNCLASSIFIABLE SUBSTANCES.

Lignin and related compounds. LI. Solvent fractionation of maple ethanol-lignin. R. F. Patterson, K. A. West, E. L. Lovell, W. L. Hawkins, and H. Hibbert. **LII. Fractionation of lignin and other polymerides.** E. L. Lovell and H. Hibbert (*J. Amer. Chem. Soc.*, 1941, **63**, 2065—2070, 2070—2073; cf. A., 1940, II, 378).—LI. The amorphous material obtained by ethanolysis of maple wood is separated by fractional pptn. into C_5H_5N-sol., Et_2O-sol. and -insol., and H_2O-sol. products, and low-boiling oils, mol. complexity (determined by η) decreasing in the order named. Analysis and the relation of η and precipitability by H_2O indicate that the Et_2O-sol. and -insol. and H_2O-sol. fractions are chemically similar. The method is probably generally applicable.

LII. Lignin is fractionated by varying the proportions of solvents in its solution in two-layer mixtures of MeOH, H_2O, $CHCl_3$, and CCl_4. R. S. C.

Pigments from marine muds.—See A., 1941, **I**, 487.

V.—HETEROCYCLIC.

Vinylfuran. M. M. Koton [with A. P. Votinov and F. S. Florinski] (*J. Appl. Chem. Russ.*, 1941, **14**, 181—186).—2-Vinylfuran (**I**) is obtained in 42% yield by distilling β-2-furylacrylic acid at 250—275°. A hard, insol., infusible polymeride of (**I**) is obtained by heating at 100° with 1% of HCl, $SnCl_4$, $SiCl_4$, $SbCl_5$, or AcCl, or at 175° with 5% of linseed oil. R. T.

Carbonyl compounds of the furan series. II. Certain derivatives of furylacraldehyde. G. E. Rudtschenko (*J. Gen. Chem. Russ.*, 1940, **10**, 1953—1957).—Furylacraldehyde and arylamines in EtOH (3 hr. at the b.p.) yield the anils $CHR{:}CH{\cdot}CH{:}NR'$ (R = *furyl*, R' = *Ph*, m.p. 65·5°, o-*tolyl*, b.p. 180—181°/6 mm., m-*tolyl*, b.p. 188—189°/8 mm., p-*tolyl*, m.p. 74·5—75°, o-*xylyl*, m.p. 49·5—50°, *mesityl*, m.p. 77—77·5°, o-*anisyl*, m.p. 77·5—78°, p-*anisyl*, m.p. 66°). With *p*-$C_6H_4(NH_2)_2$ or benzidine the products are *p*-$C_6H_4(N{:}CH{\cdot}CH{:}CHR)_2$, m.p. 188°, or $(C_6H_4{\cdot}N{:}CH{\cdot}CH{:}CHR)_2$, m.p. 197—198° (decomp.). R. T.

1 : 2-Pyrone-5-carboxylamides.—See B., 1941, III, 269.

Derivatives of coumaran. VIII. Reductions in the coumaranone series. Synthesis of dihydrotubanol. R. L. Shriner and M. Witte (*J. Amer. Chem. Soc.*, 1941, **63**, 2134—2137; cf. A., 1941, II, 201).—4-Hydroxy-2-*iso*propylidenecoumaran-3-one (**I**) and H_2–PtO_2 in abs. EtOH at 45 lb./room temp. give 4-*hydroxy*-2-iso*propylcoumaran*-3-*one* (**II**) (98·5%), m.p. 92° (*hetazine*, m.p. 220°), which with (*a*) boiling Ac_2O, (*b*) BzCl and Na_2CO_3 in boiling 1 : 1 H_2O–$COMe_2$, or (*c*) PhNCO at 100° gives (*a*) the 4-*acetate*, b.p. 147°/3 mm., of (**II**) and 3 : 4-*diacetoxy*-, m.p. 72—74°, b.p. 175°/3 mm., and (*b*) 3 : 4-*dibenzoyloxy*-2-iso*propylbenzfuran*, m.p. 132°, and (*c*) the corresponding 3 : 4-*bisphenylurethane*, m.p. 220°. However, in presence of a little HCl, (**I**) absorbs 5 H_2 and gives 4-*hydroxy*-2-iso*propylhexahydrocoumaran*, b.p. 130°/4 mm. (*phenylurethane*, m.p. 181—182°, obtained only at 100°). With H_2–Raney Ni at 60°/1300 lb. in abs. EtOH, (**I**) gives 3 : 4-*diethoxy*-, b.p. 115°/3 mm., or in dry dioxan at 100°/2700 lb. 3 : 4-*dihydroxy*-2-iso*propyloctahydrobenzfuran*, m.p. 134° (*bisphenylurethane*, m.p. 192°). 4-Benzoyloxy-2-*iso*propylidenecoumaran-3-one and H_2–PtO_2 in HCl–EtOH at 25°/42 lb. similarly give *dihydrotubanol hexahydrobenzoate* (68%), b.p. 170°/2 mm., hydrolysed by NaOH–EtOH–H_2O to dihydrotubanol (*phenylurethane*, m.p. 137°). R. S. C.

Coumarone derivatives.—See B., 1941, II, 408.

Effect of substitution in 7-hydroxycoumarin on the elimination of the pyrone ring by caustic alkali. D. B. Limaye and K. M. Kulkarni (*Rasāyanam*, 1941, **1**, 208—214).—7-Hydroxycoumarin is converted by NaOH at 70° into 2 : 4 : 1-$C_6H_3(OH)_2{\cdot}CH{:}CH{\cdot}CO_2H$; *m*-$C_6H_4(OH)_2$ (**I**) does not appear to be produced, indicating the absence of ring elimination. Similar results are obtained at 100°, whereas a small proportion of (**I**) results from the use of 30% alkali. 7-Methoxycoumarin is hydrolysed to a small proportion of 2 : 4 : 1-$OH{\cdot}C_6H_3(OMe){\cdot}CH{:}CH{\cdot}CO_2H$, but no *m*-$OH{\cdot}C_6H_4{\cdot}OMe$ (**II**). 7-Hydroxy-4-methylcoumarin is unchanged by 1 mol. of N-NaOH; with 2 mols. there is a small and with 4 mols. a complete elimination of the ring. Similar results are obtained with 2N-alkali, showing the reaction to depend on the proportion and not on the concn. of alkali. 7-Methoxy-4-methylcoumarin is hydrolysed to 2 : 4 : 1-$OH{\cdot}C_6H_3(OMe){:}CMe{:}CH{\cdot}CO_2H$ with a small proportion of (**II**). At 70° with 3 mols. of NaOH 7-hydroxy-8-acetyl-4-methylcoumarin (**III**) undergoes elimination as well as opening of the pyrone ring, forming 2 : 1 : 3-$C_6H_3Ac(OH)_2$ and 2 : 4 : 3-$(OH)_2C_6H_2Ac{\cdot}CMe{:}CH{\cdot}CO_2H$; with >3 mols. of NaOH (**III**) is partly unchanged and partly undergoes ring elimination, a very small amount of an alkali-sol. product, m.p. 219°, being also obtained. 7-Hydroxy-4-methylcoumarin-8-carboxylic acid, from γ-resorcylic acid and $CH_2Ac{\cdot}CO_2Et$, and 2 mols. of N-alkali hydroxide give considerable unchanged material and an unidentified monocarboxylic acid, m.p. 164°, which gives a dark blue colour with $FeCl_3$; with 4 mols. of alkali a small amount of (**I**) results by elimination of the pyrone ring. Hydrolysis of 7-methoxy-4-methylcoumarin-8-carboxylic acid with 4—5 mols. of N-alkali hydroxide yields 3 : 2 : 1-$CO_2H{\cdot}C_6H_3(OMe){\cdot}CMe{:}CH{\cdot}CO_2H$ but no β-resorcylic acid Me_1 ether. 7 : 8-Dimethoxy-4-methylcoumarin is very resistant to alkaline hydrolysis. Elimination of the pyrone ring is not observed with 7-hydroxycoumarin-4-acetic acid and 1 mol. of N-alkali hydroxide; it is evident when 2 mols. are used and almost complete with a large excess of alkali. Ring elimination does not take place when 7-methoxycoumarin-4-acetic acid is acted on by an excess of alkali. 7 : 8-Dihydroxycoumarin-4-acetic acid suffers ring elimination when boiled with 4 mols. of NaOH but the 7 : 8-$(OMe)_2$-compound is resistant to boiling alkali hydroxide. H. W.

***iso*Coumarin derivatives. I. Synthesis of *iso*coumarin-3-carboxylic acid.** N. N. Voroshcov, jun., and L. N. Bogusevitsch (*J. Gen. Chem. Russ.*, 1940, **10**, 2014—2016).—Me_2 homophthalate is condensed with $Me_2C_2O_4$ in Et_2O in presence of Na (48 hr. at room temp.); the oily product, heated at 100° for 2 hr., yields *Me*$_2$ iso*coumarin*-3 : 4-*dicarboxylate*, m.p. 134°. This with conc. HCl (2 hr. at the b.p.) gives *iso*coumarin-3-carboxylic acid. R. T.

Chemical investigation of Indian lichens. II. Synthetic uses of some lichen acids. V. V. K. Sastry and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1940, **12**, A, 498—506).—Atronorin, extracted from the lichen, *Parmelia abessinica* (Kremp.) (**I**) with light petroleum, is hydrolysed to Et hæmotommate (**II**), m.p. 113—114°, which is obtained in better yield from Et orsellinate (**III**) [from lecanoric acid obtained from (**I**)] and $Zn(CN)_2$–$AlCl_3$–Et_2O–HCl at 0°. (**II**) and $CH_2(CO_2Et)_2$ (**IV**) + piperidine at room temp. afford *Et*$_2$ 5-*hydroxy*-7-*methylcoumarin*-3 : 8-*dicarboxylate*, m.p. 141—142°, hydrolysed by 5% aq. KOH at room temp. to the 8-*carboxylic acid* (+0·5H_2O),

m.p. 270—271° (decomp.), which is decarboxylated by Cu-bronze and quinoline at 150—160° to 5-*hydroxy*-7-*methylcoumarin* (**V**), m.p. 215—216° (decomp.), also obtained from (**II**), (**IV**), and H_2SO_4. 5-Hydroxycoumarins, unlike the 7-OH-compounds, do not exhibit fluorescence. (**III**) with $CH_2Ac{\cdot}CO_2Et$–H_2SO_4 at 0°, or (less efficient) $AlCl_3$–$PhNO_2$ at 120—130°, affords *Et* 5-*hydroxy*-4 : 7-*dimethylcoumarin*-6-*carboxylate*, m.p. 179—180°, converted into the *acid*, m.p. 247° (decomp.), and thence 5-hydroxy-4 : 7-dimethylcoumarin, m.p. 258°, also obtained from (**III**), $CH_2Ac{\cdot}CO_2Et$, and H_2SO_4 at 90—95°. (**III**) or lecanoric acid, malic acid, and H_2SO_4 at 90—95°, yield (**V**). Orcinol reacts in the β-position with malic acid to give 7-hydroxy-5-methylcoumarin (cf. Sen *et al.*, A., 1930, 219). A. T. P.

5-Hydroxybenzopyrone group. III. 5-Hydroxy-2 : 3-dimethyl- and 5-hydroxy-2-methyl-3-ethyl-chromone. D. B. Limaye, G. S. Shenolikar, and S. S. Talwalkar. **IV. 5-Hydroxy-2-methyl-3-propylchromone.** V. K. Bhagwat and R. Y. Shahane (*Rasāyanam*, 1941, **1**, 217—220, 220—222).—III. 2-Propionylresorcinol (**I**) is converted by Ac_2O at 165—170° into its *diacetate*, m.p. 80°, and by Ac_2O and fused NaOAc at 165—170° into 5-*hydroxy*-2 : 3-*dimethylchromone* (**II**), m.p. 130° (*benzoate*, m.p. 194°), and its *acetate*, m.p. 112—113°. (**I**) is hydrolysed by boiling N-NaOH to COMeEt, CO_2, and m-$C_6H_4(OH)_2$ (**III**), by 2·5N-NaOH to (**I**) and AcOH, and by 0·5N-NaOH to γ-resorcylic acid (**IV**). 2-*n*-Butyrylresorcinol (**V**) is transformed by Ac_2O at 150—160° into a liquid *diacetate* and by Ac_2O and NaOAc at 150—155° into 5-*hydroxy*-2-*methyl*-3-*ethylchromone* (**VI**), m.p. 97° (*benzoate*, m.p. 158°), and its *acetate*, m.p. 107°. (**VI**) is hydrolysed by boiling 2·5N-NaOH to COMePr^a, (**V**), and (**III**) and by 0·5N-NaOH to (**IV**).

IV. 2-*n*-Valerylresorcinol (**VII**), NaOAc, and Ac_2O at 165—170° afford 5-*hydroxy*-2-*methyl*-3-n-*propylchromone* (**VIII**), m.p. 67°, and its *acetate*, m.p. 109°, also obtained directly from (**VIII**). Hydrolysis of (**VIII**) with boiling 0·5N-NaOH yields COMeBu^a, (**IV**), and (**III**), whilst with boiling 2·5N-NaOH (**VII**) and AcOH result. (**VIII**), PhCHO, and NaOEt in abs. EtOH at room temp. afford the *styrene* derivative, m.p. 158°. (**IX**) and anhyd. $AlCl_3$ at 160—165° afford a *compound*, $C_{15}H_{16}O_4$, m.p. 118°, which gives a red colour with $FeCl_3$ and is sol. in 0·1N-NaOH. H. W.

Simple colour reaction for detection of equol [7 : 4′-dihydroxy*iso*flavan] in mare's urine. W. Dirscherl (*Z. physiol. Chem.*, 1940, **264**, 57—63).—When heated to boiling with an equal vol. of 25% HNO_3, an aq. solution of equol gives a N-containing red ppt. ["equol-red" (**I**)], which is sol. in Et_2O, $C_6H_{11}{\cdot}OH$, aq. NaOH, or aq. NH_3. The reaction appears to be sp. (HNO_3 cannot be replaced by HNO_2, HCl, or H_2SO_4). It is inhibited by EtOH. The reaction is given only by the acidic fraction of the urine which is non-volatile in steam; acetylation of this fraction prevents the reaction but subsequent hydrolysis causes it to occur. Œstrone, œstradiol, equilin, and equilenin give yellow colours, as do many other phenols; 7 : 4′-dihydroxy*iso*flavone and its 4′-Me ether do not give the reaction. Various tocopherols give usually yellow, and occasionally red, colours; in the latter case no ppt. results and reaction occurs in presence of EtOH. Reduction ($Na_2S_2O_4$ in aq. AcOH) of (**I**), which is probably a nitrated quinone, gives a yellow substance (with $FeCl_3$ becomes red). H. B.

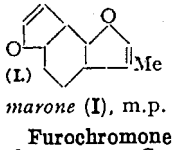
Methylation of hydroxyflavonols using methyl iodide and potassium carbonate. P. S. Rao, P. P. Reddy, and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1940, **12**, **A**, 495—497).—Quercetin, refluxed with MeI–K_2CO_3–$COMe_2$ (action is similar to CH_2N_2) for 60 hr., gives the 3 : 5 : 7 : 3′ : 4′-Me_5 derivative, m.p. 150—151°, whilst herbacetin affords the 3 : 7 : 8 : 4′-Me_4, m.p. 158—160° (sinters at 115—120°), and gossypetin yields the 3 : 7 : 8 : 3′ : 4′-Me_5 compound, m.p. 166—168°. A. T. P.

Pyrylium salts derived from 4-*o*-methylresorcylic aldehyde. L. R. Row and T. R. Seshadri (*Proc. Indian Acad. Sci.*, 1941, **13**, **A**, 510—518).—7-Methoxy-2-phenylbenzopyrylium chloride (**I**), m.p. 105—106° (cf. Perkin *et al.*, *J.C.S.*, 1908, **93**, 1098), prepared from 4-methoxysalicylaldehyde (**II**) and COPhMe–HCl–dry EtOAc, is converted by addition of NaOAc to a solution in dil. HCl, or by pouring a solution in AcOH into much H_2O, into *Ph* 2-*hydroxy*-4-*methoxystyryl ketone*, m.p. 126—128°; the latter is synthesised from (**II**) and COPhMe–KOH–MeOH. Prepared similarly to (**I**), or in EtOH–EtOAc, using ω : 4-dihydroxy-, ω : 3 : 4-triacetoxy-, or ω : 3 : 4 : 5-tetra-acetoxy-acetophenone, are 3 : 4′-*di*- (**III**), m.p. 250—251°, 3 : 3′ : 4′-*tri*- (**IV**), m.p. 258—260° (decomp.), or 3 : 3′ : 4′ : 5′-*tetra-hydroxy*-7-*methoxy*-2-*phenylbenzopyrylium chloride* (**V**), does not melt at 340°, respectively. All the pyrylium salts exhibit strong greenish fluorescence in conc. H_2SO_4, persisting on addition of H_2O in cases of (**I**) and (**III**). Numerous colour reactions are recorded, using a range of buffered solutions. (**III**), (**IV**), and (**V**) in general resemble pelargonidin, cyanidin, and delphinidin, although they show a marked poverty of colour in reactions. A. T. P.

Structure of cannabidiol. XII. Isomerisation to tetrahydrocannabinols. R. Adams, C. K. Cain, W. D. McPhee, and R. B. Wearn (*J. Amer. Chem. Soc.*, 1941, **63**, 2209—2213; cf. A., 1941, II, 331).—Isomerisation of cannabidiol (**I**) by *p*-$C_6H_4Me{\cdot}SO_3H$ in boiling C_6H_6 or by a drop of H_2SO_4 in boiling *cyclo*hexane gives *tetrahydrocannabinol* (**II**), b.p. 169—172°/0·03 mm., $[\alpha]_D^{28}$ ~ −265° in 95% EtOH or $COMe_2$. Boiling, dry 0·5M-HCl–EtOH gives an *isomeride* (**III**), b.p. 157—160°/0·05 mm., $[\alpha]_D^{26}$ −130±5° in 95% EtOH. Seven other acids effected partial cyclisation or none. (**II**) and (**III**) are considered to be pure isomerides, products of intermediate [α] (A., 1940, II, 379) being mixtures. In dry Et_2O at 0°, (**III**) adds HCl to give an oil, $[\alpha]_D^{26}$ −82° in 95% EtOH, unaffected by dil., aq. $NaHCO_3$ but decomposed, when distilled, to HCl and an oil, $[\alpha]_D^{26}$ −196° to −203° in 95% EtOH. (**II**) gives no such adduct, which confirms the view that isomerism is due to the position of the ethylenic linking. Isomerisation of (**III**) or other material of low [α] by *p*-$C_6H_4Me{\cdot}SO_3H$ gives products of intermediate [α], indicating that shift of the nuclear C:C of (**I**) takes place during or before cyclisation. Absorption spectra of (**I**), (**II**), and (**III**) are very similar but differ from that of the H_4-derivative in which the ethylenic linking is conjugated with the C_6H_6 ring. Cannabidiol Me_2 ether and 2·5% O_3 in AcOH give an ozonide, which in warm H_2O yields CH_2O (confirmation of the $CMe{:}CH_2$) and indefinite aldehydes and with CrO_3–AcOH gives 2 : 6-dimethoxy-4-*n*-amylbenzaldehyde (2 : 4-*dinitrophenylhydrazone*, m.p. 228—230°); with 8% O_3 (excess) n-$C_5H_{11}{\cdot}CO_2H$ is obtained. Dihydrocannabidiol and *p*-$C_6H_4Me{\cdot}SO_3H$ in boiling C_6H_6 give *olivetol Me$_2$ ether*, b.p. 100—103°/0·05 mm., and a resin (? polymerised menthadiene). Hydrogenation (PtO_2) of H_4-derivatives of any [α] gives the H_6-compound, $[\alpha]_D$ −70°. Attempts to prepare cryst. derivatives of (**II**) or OH-derivatives of dihydrocannabidiol Me_2 ether failed. The marihuana effect of (**II**) on dogs is approx. equal to that of (**III**). (**II**) has typical marihuana effect on humans, thus confirming the validity of tests on dogs. R. S. C.

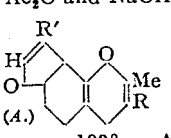
Aminoeuxanthic acid.—See A., 1941, III, 930.

Furocoumarone group. I. Synthesis of 3 : 3′-dimethyl-6′ : 7′-furocoumarone. D. B. Limaye and T. B. Panse (*Rasāyanam*, 1941, **1**, 231—232).—The dry Na salt of 6-hydroxy- is converted by $CH_2Br{\cdot}CO_2Et$ and NaOEt in boiling EtOH into 6-*carboxymethoxy*-7-*acetyl*-3-*methylcoumarone*, m.p. 167° (decomp.) (*Et* ester, m.p. 48°), converted by NaOAc and Ac_2O at 150—155° into 3 : 4′-*dimethyl*-(2′ : 3′-6 : 7)-*furocoumarone* (**I**), m.p. 27°, b.p. 270°. H. W.



(I.)

Furochromone group. I. Furochromones from hydroxychromones. G. R. Kelkar and D. B. Limaye (*Rasāyanam*, 1941, **1**, 228—230).—The dry Na salt of 7-hydroxy- is transformed by $CH_2Br{\cdot}CO_2Et$ at 160—165° into 7-*carbethoxymethoxy*-8-*acetyl*-2 : 3-*dimethylchromone*, m.p. 137—139°, hydrolysed by boiling 0·1N-NaOH to the *acid*, m.p. 240° (decomp.), which passes when heated above its m.p. or with Ac_2O and NaOAc at 160—170° into 2 : 3 : 4′-*trimethyl*-(2′ : 3′-7 : 8)-*furochromone* (cf. *A*), m.p. 245°. Similarly 6-*carboxymethoxy*-8(6)-*benzoyl*-2-*methylchromone*, m.p. 260° (decomp.), passes at 260—265° or 150—165° in presence of NaOAc and Ac_2O into 4′-*phenyl*-2′-*methyl*-(2′ : 3′-7 : 8)-*furochromone* (cf. *A*), m.p. 193°. Analogously, 4′-*phenyl*-2 : 3-*dimethyl*-(2′ : 3′-7 : 8)-*furochromone*, m.p. 153—155°, is derived from 7-*carboxymethoxy*-8(6)-*benzoyl*-2 : 3-*dimethylchromone*, m.p. 225° (decomp.), and 2 : 4′-*dimethyl*-(2′ : 3′-7 : 8)-*furochromone* from 7-*carboxymethoxy*-8-*acetyl*-2-*methylchromone*, m.p. 273° (decomp.). H. W.



(A.)

Absorption spectra of derride, *iso*rotenone, malaccol, toxicarol, and sumatrol.—See A., 1941, I, 446.

Saponins and sapogenins. XVIII. Non-identity of chlorogenonic, digitogenic, and digitoic acids. C. R. Noller and S. Lieberman (*J. Amer. Chem. Soc.*, 1941, **63**, 2131—2134; cf. A., 1941, II, 264).—The dibasic CO-acid (termed *chlorogenonic acid*) (I), $C_{27}H_{40}O_7$, +AcOH, m.p. 235—237° or (usually) 229—230° (shrinks at 225°), $[\alpha]_D^{25}$ −40·6°, $[\alpha]_{5461}^{25}$ −51·3° in dioxan (Me_2 ester, new m.p. 159·5—160·5°, $[\alpha]_D^{23}$ −45·1°, $[\alpha]_{5461}^{23}$ −54·0° in dioxan; fairly sol. Mg salt does not crystallise from 95% EtOH), obtained (A., 1937, II, 346) by oxidation of chlorogenin, is stable towards alkali and differs from digitogenic, +AcOH, m.p. 215·5—217·5° (sinters at 170—175°) or (preheated bath) 183°, $[\alpha]_D^{23}$ −41·2°, $[\alpha]_{5461}^{23}$ −47·6° in dioxan (Me_2 ester, sinters at 153°, m.p. 154·4—159·5°, $[\alpha]_D^{23}$ −49·4°, $[\alpha]_{5461}^{23}$ −54·8° in dioxan), and digitoic acid (anhyd.), sinters at 205°, m.p. 207—209°, $[\alpha]_D^{25}$ −85·7°, $[\alpha]_{5461}^{25}$ −130·9° in dioxan (cryst. Mg salt from 95% EtOH) (cf. Marker *et al.*, A., 1940, II, 99). Na–EtOH–N_2H_4,H_2O at 200° converts (I) into gitogenic acid, thus confirming oxidative fission of the $C_{(2-3)}$ linking. The positions of the OH are in doubt. Digitogenin is obtained having m.p. 289—293° (shrinks at 285°). R. S. C.

Thiophen series. LIII. 2 : 2′-Di-α-thiophanthrenequinonyl, the thiophen isologue of 2 : 2′-dianthraquinonyl. W. Steinkopf and M. Kühnel (*Annalen*, 1940, **545**, 33—37).—2 : 2′-Dithienyl, o-$C_6H_4(CO)_2O$, and $AlCl_3$ in boiling CS_2 give 5-o-*carboxybenzoyl*-, m.p. 176·5°, and 5 : 5′-*di*-o-*carboxybenzoyl*-2 : 2′-*dithienyl* (I), m.p. 300°, separable owing to the insolubility of (I) in boiling PhMe. $AlCl_3$–NaCl and (I) at 210° afford 3—4% of 2 : 2′-*di*-α-*thiophanthrenequinonyl* [4 : 5 : 4′ : 5′-*diphthalyl*-2 : 2′-*dithienyl*] (II), sublimes at >360°/high vac., m.p. 498° (uncorr.), 507° (corr.), which gives a wine-red vat (alkaline $Na_2S_2O_4$), is luminescent (golden-orange) in Hg-light, and is largely unaffected by Zn dust–$ZnCl_2$–NaCl at 370°/45 min. Conversion of (I) into (II) could not be effected with conc. H_2SO_4, PCl_5, or $AlCl_3$. 5 : 5′-Dimethyl-2 : 2′-dithienyl and o-$C_9H_4(CO)_2O$ give (as above) the 3 : 3′-*di*-o-*carboxybenzoyl* derivative (+H_2O), m.p. 147°, ring-closure of which could not be effected. 5-*Phenyl*-2-2′-*quinolylthiophen*, m.p. 144—145·5°, is obtained by distillation of its 4′-CO_2H-derivative (A., 1940, II, 232) with soda-lime. H. B.

Theory of hydrolysis of amines. 2 : 6-Diaminopyridine and 2-amino-6-hydroxypyridine. A. I. Titov and B. B. Levin (*J. Gen. Chem. Russ.*, 1941, **11**, 9—15).—The velocity of hydrolysis by 70% H_2SO_4 at 100° falls in the order 2 : 6-diamino- (I) > 2-amino-6-hydroxy- > 2-amino-pyridine. This is explained on lines of resonance mesomerism. The first product of hydrolysis of (I) is 2 : 6-dihydroxypyridine (Ac_2 derivative, m.p. 69°). Rupture of the C_5H_5N ring also takes place during hydrolysis, with production of glutaconic acid. R. T.

2-Picolinoylanilides.—See B., 1941, II, 408.

Preparation of nicotinic acid from pyridine. S. M. McElvain and M. A. Goese (*J. Amer. Chem. Soc.*, 1941, **63**, 2283—2284).—Nicotinic acid is readily prepared from 3-bromopyridine by the action of CuCN (1·5 mol.) at 165—170°, and hydrolysis (90%) of the 3-cyanopyridine (50%) by boiling NaOH (4 g.) in 70% EtOH (40 ml.). R. S. C.

***N*-4-Nicotinylsulphanilamide.**—See B., 1941, III, 296.

Monothiophthalimide and some derivatives of oxindole. J. C. Porter, (Sir) R. Robinson, and M. Wyler (*J.C.S.*, 1941, 620—624).—o-$C_6H_4(CN)_2$ and NaSH give o-*cyanothiobenzamide*, decomp. ~218°, which with HCl affords *monothiophthalimide* (I), m.p. 175°. Condensation of (I) with the appropriate reagent affords *anilophthalimidine*, m.p. 170°, *anhydrophthalimide*-N-*methyloxindole*, m.p. 242°, β-quinophthaline, and bismetaindolone (with α-$C_{10}H_7$·OH), and with NH_2·SO_3NH_4 and $CuCl_2$ a *phthalocyanine* is obtained. *N*-Methyloxindole (II) and $Et_2C_2O_4$ with Na–EtOH yield *Et* N-*methyloxindole*-3-*oxalate*, m.p. 81° (*phenylhydrazone*, m.p. 158·2°), which condenses with p-C_6H_4Me·NH_2 to a *compound*, $C_{20}H_{20}O_3N_2$, m.p. 97°, and with the appropriate reagent to p-*nitrobenzeneazo*-, m.p. 272°, 3-*vanillylidene*-, m.p. 180·5°, and 3-p-*dimethylaminobenzylidene*-N-*methyloxindole*, m.p. 155°. 3-Formyl-*N*-methyloxindole and $NPhMe_2$ give a *compound*, m.p. 236°. (*N*-methyloxindolylmethyleneoxindole?). 6-Aminopiperonal and (II) with KOH give 3-(6′-*aminopiperonylidene*)-N-*methyloxindole*, m.p. 186°, which with NH_2·SO_3H and quinoline yields 2 : 3-*methylenedioxy*-10-*methylquinindoline*, m.p. 225°. Nitration (KNO_3–H_2SO_4) of (II) leads to 6(or 5)-*nitro*-N-*methyloxindole*, m.p. 196°, reduced ($SnCl_2$–HCl) to the -NH_2-compound, m.p. 112·5°. Cotarnine and (II) give *anhydrocotarnine*-N-*methyloxindole*, m.p. 154·5° (decomp.), and with isatin-α-anil, *N*-methylindirubin, m.p. 283°, is obtained. The Me derivative of acet-p-anisidide and CH_2Cl·COCl, followed by $AlCl_3$, yields 5-*hydroxy*-N-*methyloxindole*, m.p. 186·5°, which is methylated to the *OMe*-compound, m.p. 92°. (II) and OPh·$[CH_2]_2$·Br give a *substance*, $C_{20}H_{24}O_4N_2$, m.p. 233°. 5-Hydroxy-*N* : 3-dimethyloxindole and OPh·$[CH_2]_2$·Br afford 5-methoxy-1 : 3-dimethyl-3-β-phenoxyethyl-2-indolinone. F. R. S.

Quinoline derivatives. W. S. Emerson and J. W. Davis (*J. Amer. Chem. Soc.*, 1941, **63**, 2279).—1 : 2-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline zincichloride*, m.p. 152—154°, and *hydriodide*, m.p. 138·5—140°, and 2 : 6 : 8-*trimethylquinoline zincichloride*, m.p. ~200°, are prepared. R. S. C.

Sympathomimetics. II.—See A., 1941, II, 360.

Separation of Acriquin [Atebrine] into optical antipodes. G. V. Tschelincev znd E. D. Osetrova (*J. Gen. Chem. Russ.*, 1940, **10**, 1978—1980).—6-Chloro-9-(δ-diethylamino-α-methylbutyl)amino-2-methoxyacridine (I) in EtOH and bromocamphorsulphonic acid yield a 1 : 2 *salt*, m.p. 170—172°, $[\alpha]_D$ −195·5° in EtOH, from which the *l*-isomeride of (I), an oil, $[\alpha]_D$ −194·5° in EtOH, is isolated as the *dihydrochloride*, m.p. 243° (decomp.), $[\alpha]_D$ −357° in H_2O. The *d*-isomeride, an oil, $[\alpha]_D$ +197° in EtOH [*dihydrochloride*, m.p. 243° (decomp.), $[\alpha]_D$ +358·6° in H_2O)], is isolated from the mother-liquor from the *l*-salt. R. T.

Synthesis of *ms.*[4 : 5]-benzacridan. H. Waldmann and S. Back (*Annalen*, 1940, **545**, 52—58).—N-o-*Nitrophenyl*-α-*naphthylamine*, m.p. 155° (from o-C_6H_4Br·NO_2, α-$C_{10}H_7$·NH_2, and anhyd. NaOAc at 222—226°), is reduced (EtOH–Na_2S or EtOH–conc.HCl–$SnCl_2$) to the o-NH_2-derivative, m.p. 135°, which with $NaNO_2$ in aq. AcOH–H_2SO_4 at −8° followed (after 10 min.) by H_2O at ≯−3° gives 1-α-*naphthylbenztriazole* (I), m.p. 114°. Thermal decomp. of (I) affords α-naphthocarbazole; no decomp. occurs in boiling $NHPh_2$. 1 : 8-$C_{10}H_6(NH_2)_2$, NH_2Ph, and a little I at 230°/6 hr. and then at 250°/2 hr. give *N-phenyl*-1 : 8-*naphthylenediamine*, b.p. 253°/14 mm., m.p. 133°, converted by $NaNO_2$ in aq. AcOH at ≯−2° into 1-*phenyl*peri*naphthtriazole*, m.p. 134°, which decomposes in boiling $C_{10}H_8$ or (explosively) at 180° alone yielding ms.[4 : 5]-*benzacridan*, m.p. 123°. 1-2′ : 4′-*Dinitrophenyl*peri*naphthtriazole*, decomp. 163°, in boiling $PhNO_2$ yields 7 : 9-*dinitro*-ms.[4 : 5-]*benzacridan*, decomp. 293°, whilst 1-2′ : 4′-dinitrophenylbenztriazole in $PhNO_2$ at 300° (sealed tube) gives 1 : 3-*dinitrocarbazole*, m.p. 266°. *peri*Naphthtriazole decomposes at 236—237° (rapid heating). H. B.

Preparation of 5-phenylhydantoin-5-acetates and -acetamides. B. G. Rogers and H. R. Henze (*J. Amer. Chem. Soc.*, 1941, **63**, 2190—2191).—CH_2Bz·CO_2Et, KCN, and $(NH_4)_2CO_3$ in 60% EtOH at 58—60° give *Et* 5-*phenylhydantoin*-5-*acetate* (60%), m.p. 139—140°, hydrolysed by boiling 20% HCl to the corresponding *acid* (I), m.p. 261·5—262·5° (decomp.), and with aq. NH_3 or NH_2Et at room temp. (7—10 days) giving the *amide* (77%), m.p. 255·5—256·5° (decomp.), and *ethylamide* (33%), m.p. 247—248° (decomp.), respectively. Attempts to prepare other amides similarly failed, but the *diethylamide* (65%), m.p. 223—223·5°, *morpholide* (70%), m.p. 168—170°, resolidifies, remelts at 255·5—257°, and *anilide* (62%), m.p. 269—270°, are obtained by way of the acid chloride ($SOCl_2$). With boiling HCl–ROH, (I) gives the *Me*, m.p. 223—224°, *Pr*$^{\alpha}$, m.p. 105·5—107°, iso*amyl*, m.p. 126·5—127·5°, *allyl*, m.p. 112·5—113·5°, *OH*·$[CH_2]_2$, m.p. 127—128°, and CH_2Ph ester, m.p. 160—161°. The *Ph* ester, m.p. 226—227°, is obtained from the acid chloride and PhOH in C_5H_5N–$(CCl_2^{\cdot})_2$. CH_2Bz·CN, KCN, and $(NH_4)_2CO_3$ in 65% EtOH react incompletely at 58—62°, giving 9% of 5-*phenylhydantoin*-5-*acetonitrile*, m.p. 251·5—252·5° (decomp.). No product was obtained from CHMeBz·CN. CHMeBz·CO_2Et gives 32% of *Et* 5-*phenylhydantoin*-5-α-*propionate*, m.p. 241—242°, hydrolysed by 1 : 1 aq. HCl to the corresponding *acid*, m.p. 271·5—273°. M.p. are corr. R. S. C.

Ultra-violet absorption spectra of 5-methoxy-1-phenyl-3-methylpyrazole and 1-phenyl-3-methyl-5-pyrazolone.—See A., 1941, I, 446.

Action of copper compounds on 5-methyl-2-thiobarbituric acid. T. Nisikawa (*Mem. Ryojun Coll. Eng.*, 1940, **13**, 195—235).—5-Methylthiobarbituric acid (I) (1 mol.) and $Cu(OAc)_2$ (1·2 mols.) or $Cu(OH)_2$ in boiling H_2O give a red ppt. converted by boiling ~2N-HCl into a yellow *complex* (II), $(C_5H_5O_2N_2S)_2,(C_5H_4O_2N_2SCu)_2,2HCl$. Boiling H_2O resolves

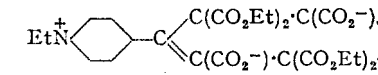
(**II**) into the sol. *di*-(4 : 6-*diketo*-5-*methyl*-3 : 4 : 5 : 6-*tetrahydro*-2-*pyrimidyl*) *disulphide* (**III**), m.p. 298° (decomp.) (sinters and darkens at 285°) (no colour with $FeCl_3$; contains 6·6% of enolic form in ? 0·005N-MeOH solution), and its red insol. *Cu* salt [also formed from (**III**) and Cu_2O in boiling EtOH; stable to H_2SO_4 and 3N-NaOH; converted by conc. HCl at room temp. into (**II**); oxidised by HNO_3 to *di*-(2 : 4 : 6-*triketo*-5-*methylhexahydro*-5-*pyrimidyl*) *ether*, chars at >300°]. The reactions etc. of (**III**) and its Cu^I salt indicate that they are resonance hybrids. Oxidation (H_2O_2; aq. EtOH–I) of (**I**) gives no (**III**) but affords 5-*hydroxy*-5-*methylthiobarbituric acid*, m.p. 233·5°, obtained pure only with difficulty. Cu^I 4-imino-5-methylthiobarbiturate and NaOH form a complex (**IV**), $C_5H_6ON_3SCu,C_5H_7ON_3S,NaOH$, which with (**I**) in warm ~2N-HCl yields a *complex* (**V**), $C_5H_6ON_3SCu,C_5H_6O_2N_2S,HCl$, also obtained in a less pure condition by the direct action of aq. HCl on (**IV**), whereby an intermediate *complex*, $C_5H_6ON_3SCu,C_5H_7ON_3S,HCl$, can be isolated. Boiling 8N-HCl hydrolyses (**IV**) to Cu^I 5-*methylthiobarbiturate hydrochloride* (**VI**), $(C_5H_5O_2N_2SCu,HCl)_2$, best prepared from (**I**) and Cu_2O in 0·8N-aq. NH_3 at ~43° followed by aq. HCl (final concn. ~2N.), which with 4-imino-5-methylthiobarbituric acid in aq. NaOH followed by 2N-HCl gives (**V**). Aq. NaOH converts (**V**) into (**IV**) and (**I**). Titration of (**VI**) with NaOH (phenolphthalein) shows that it functions as a dibasic acid and is thereby converted into Na Cu^I 5-methylthiobarbiturate, which when dried at 115° undergoes oxidation to *Na hydroxycupric* 5-*methylthiobarbiturate* (**VII**), $[C_5H_4O_2N_2SNaCu(OH)]_2$. Suitable treatment of (**VII**) with aq. HCl affords a complex, $(C_5H_5O_2N_2ClSCu)_2,xH_2O$ [also formed together with the Cu^I salt of (**III**) from (**I**), $Cu(OAc)_2$ or $Cu(OH)_2$, and dil. HCl], which is converted by boiling ~2N-HCl (whereby some O_2 is evolved) or by drying at 115° into Cu^{II} 5-*methylthiobarbiturate hydrochloride* (**VIII**), $(C_5H_5O_2N_2SCu,HCl)_2$; in the former case (**VIII**) may be accompanied by some of the *complex*, $(C_5H_5O_2N_2SCu)_2S,2HCl$. (**VIII**) is also obtained from (**I**) and $Cu(OH)_2$ or Cu_2O in 10N. aq. NH_3 followed by aq. HCl; in 0·8N. aq. NH_3 (cf. above) (**VI**) is the ultimate product, whilst in 3·6N. aq. NH_3 a mixture of (**VI**) and (**VIII**) results. When kept in contact with H_2O at 40°, (**VI**) gives Cu^I 5-*methylthiobarbiturate hydrate* (**IX**), $(C_5H_5O_2N_2SCu,H_2O)_2$ [regenerates (**VI**) with aq. HCl], which undergoes oxidation and dehydration at 127° to Cu^{II} 5-*methylthiobarbiturate* (**X**) [*hydrate*, $(C_5H_5O_2N_2SCu,H_2O)_2$, obtained by exposure of (**X**) to H_2O vapour at 65° or from (**VIII**) in contact with H_2O at 42°]. (**IX**) is also prepared from (**I**) and Cu_2O in dil. aq. NH_3 followed by H_2SO_4. (**VIII**) appears to exist in orange and brown forms. Prolonged heating of (**VII**) and (**X**) at 145° gives the *substances*, $(C_5H_4O_2N_2SNaCu)_2O$ and $(C_5H_5O_2N_2SCu)_2O$ (impure), respectively. The f.p., p_H, and conductivities of aq. solutions of the Na Cu complexes are determined. Constitutions are assigned to many of the complexes. H. B.

Thiobarbituric acids.—See B., 1941, **III**, 270.

Pyrimidines. CLXXIII. Interaction of chloromethyl ether with 4-methyluracil. II. (Miss) M. M. Endicott and T. B. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 2063—2065; cf. A., 1941, II, 270).—4-Methyluracil and $CH_2Cl{\cdot}OMe$ at 100° (much less well 80—85° or 125—130°) give variable yields of 4-*methyl*-5-*chloromethyluracil* (**I**), decomp. 330—335° (yellow at 225°), with small amounts of an insol. mixture of di-4-methyl-2 : 6-dihydroxy-5-pyrimidylmethane (**II**) and (?) a polymeride of 4-methyl-5-hydroxymethyluracil. The structure of (**I**) is proved by conversion by AgOAc in boiling AcOH into the 5-$CH_2{\cdot}OAc$ compound. The Cl of (**I**) is ionic, reacting with aq. $AgNO_3$. With NaOR–ROH at the b.p., (**I**) gives 4-*methyl*-5-*ethoxy*-, sinters at 195—200°, decomp. 312—315°, and -*methoxymethyl*-*uracil*, decomp. >330°, and with H_2O or, better, NaOH (1 mol.) gives 4-*methyl*-5-*hydroxymethyluracil*, m.p. 314—315° (decomp.). Conc. HCl converts (**I**) into (**II**), but 4-chloromethyl- and 5-methyl-4-chloromethyl-uracil are unaffected. R. S. C.

Substituted 2-sulphanilamidopyrimidines. W. T. Caldwell, E. C. Kornfeld, and C. K. Donnell (*J. Amer. Chem. Soc.*, 1941, **63**, 2188—2190).—$COR{\cdot}CH_2R'$, HCO_2Et, and Na in Et_2O give good yields of $COR{\cdot}CR':CH{\cdot}OH$, which with guanidine carbonate in boiling Et_2O give 2-amino- (from *cyclo*hexanone; 23%), 2-amino-5-methyl-8-*iso*propyl- (from menthone; 32%), and 2-amino-8-methyl-5 : 8-*endoiso*propylidene- (from camphor; 64% obtained by condensation in $C_5H_{11}{\cdot}OH$ with continuous removal of H_2O) -5 : 6 : 7 : 8-tetrahydroquinazoline, 2-amino-4 : 5-dimethyl- (from COMeEt; 6·1%), -4-*methyl*-5-n-*amyl*- (**I**), m.p. 92—93° (from $COMe{\cdot}C_6H_{13}$-*n*; 4·4%; 20% of impure product formed in Pr^{β}_2O with removal of H_2O), and -4 : 5-trimethylene-pyrimidine (from *cyclo*pentanone; very poor yield). The structure of (**I**) follows from its oxidation by HNO_3 (*d* 1·6) in H_2SO_4 at 0°, without nitration, to 2-*amino*-5-n-*amylpyrimidine*-4-*carboxylic acid*, m.p. 191—192°. Condensation of the products with *p*-$NHAc{\cdot}C_6H_4{\cdot}SO_2Cl$ in C_5H_5N at 60° and later hydrolysis by boiling 0·5—1·0N-NaOH gives 2-*sulphanilamido*-, m.p. 255—256° (N^4-*Ac* derivative, m.p. 258—260°), 2-*sulphanilamido*-5-*methyl*-8-*iso*propyl-, m.p. 185—187° (N^4-*Ac* derivative, m.p. 227·5—228·5°), and 2-*sulphanilamido*-8-*methyl*-5 : 8-endoiso-*propylidene*-, m.p. 276—277° (N^4-*Ac* derivative, +3H_2O, m.p. 261·5—262°), -5 : 6 : 7 : 8-*tetrahydroquinazoline*, 2-*sulphanilamido*-4 : 5-*dimethyl*-, m.p. 225·7—226·3° (N^4-*Ac* derivative, m.p. 276—277°), -4-*methyl*-5-n-*amyl*-, m.p. 188—190° (N^4-*Ac* derivative, m.p. 208·3—209°), and -4 : 6-*dimethyl*-, m.p. 178—180° (N^4-*Ac* derivative, m.p. 246·8—247·4°), -*pyrimidine*. These products are moderately to very sol. in H_2O and form sol. hydrochlorides and Na salts. M.p. are corr. R. S. C.

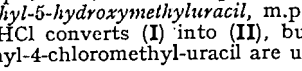
Condensation of α-picoline and quinaldine with active ketones. S. M. McElvain and H. G. Johnson (*J. Amer. Chem. Soc.*, 1941, **63**, 2213—2217).—2-Methylpyridine with $CO(CO_2Et)_2$ at 140° gives Et_2 2-*pyridylmethyltartronate* (**I**) (33%), m.p. 38—39°, b.p. 148—150°/1 mm., with $COBz_2$ gives *αα-dibenzoyl*-β-2-*pyridylethyl alcohol* (16%), m.p. 115—116°, with $COBz{\cdot}CO_2Et$ (modified prep.), b.p. 106—110°/1 mm., gives *Et α-hydroxy*-α-*benzoyl*-β-2-*pyridylpropionate* (74%), m.p. 100—101°, with Bz_2 (at 175°) gives α-*benzoyl*-α-*phenyl*-β-2-*pyridylethyl alcohol* (54%), m.p. 110—111°, and with alloxan hydrate gives 5-*hydroxy*-5-2′-*pyridylmethylbarbituric acid* (30%), m.p. 230—231°. Quinaldine gives similarly Et_2 2-*quinolylmethyltartronate* (47%), m.p. 70—71°, *αα-dibenzoyl*-β-2-*quinolylethyl alcohol* (24%), m.p. 258—260°, *Et α-hydroxy*-α-*benzoyl*-β-2-*quinolylpropionate* (**II**) (4%), m.p. 80—81°, and 5-*hydroxy*-5-2′-*quinolylmethylbarbituric acid* (24%), m.p. 238—240°, but with Bz_2 (at 175°) gives *Ph α-phenyl*-β-2-*quinolylvinyl ketone* (38%), m.p. 187—188°. Low yields are due to formation of other (tarry) condensation products. Thus, 54% of (**II**) is obtained in boiling dioxan, and (**I**) is accompanied by 40% of *Et* β-2-*pyridylacrylate*, m.p. 26—27°, b.p. 104—105°/0·7 mm., and 8% of the dibetaine (? **III**), m.p. 258—260° (decomp.) (method of formation discussed). The



(**III.**)

structure of (**III**) is supported by cryoscopy in C_6H_6, failure to react with EtI, formation of a *ferricyanide*, +2H_2O, m.p. >320°, decolorisation of aq. $KMnO_4$ and Br, interaction with conc. aq. NH_3 at room temp. to give a Et_2 ester *diamide*, $C_{30}H_{32}O_{10}N_4$, m.p. 282—284°, formation in boiling dry HCl–EtOH of a *dihydrochloride*, m.p. 129—130°, and later of an ester dihydrochloride, and absorption in presence of Raney Ni at 100°/112 atm. of 2 H, at 155°/112 atm. of a further 9 H, and at 160°/112 atm. of a final 9 H (hydrogenolysis to H_2O-sol. products). R. S. C.

Dithio-β-*iso*indigo (dithiodiphthalimidine) from phthalonitrile. I. Condensation reaction of *o*-dinitriles. II. Mechanism of its formation from phthalonitrile. Derivatives. III. Further members of the series. H. D. K. Drew and D. B. Kelly (*J.C.S.*, 625—630, 630—637, 637—641).—**I.** *o*-$C_6H_4(CO)_2NH$ and P_2S_5 in xylene give *mono*-, m.p. 174°, and *di*-*thiophthalimide*, m.p. >350°. *o*-$C_6H_4(CN)_2$ in EtOH–NH_3 with H_2S yields *dithio*-β-iso*indigo* (**I**),



and tautomeric forms, m.p. >350°, which forms metallic *compounds*, $C_{16}H_8N_2S_2Hg$; $C_{16}H_8N_2S_2Hg,HgCl_2,4C_5H_5N$; $C_{16}H_8N_2S_2Cu$; $C_{32}H_{16}N_4S_4Cu,4H_2O$; $C_{32}H_{18}N_4S_4Co,2H_2O$; and $C_{16}H_8N_2S_2Cd,2H_2O$. Methylation of (**I**) affords SS′-*dimethyldithio*-β-iso*indigo*, m.p. 258° (Et_2 compound, m.p. 162°), which with HCl gives the S-*methylthio*-compound, m.p. 297° (*Et* compound, m.p. 252°), further converted (HCl–EtOH) into β-*iso*indigo. (**I**) may also be obtained by condensing phthalimidine with S, dithiophthalimide (**II**) with H_2S–NH_3, and heating (**II**) with Ag. N_2H_4 and (**I**) give β-iso*indigodihydrazone*, decomp. 260°. 3 : 6-Dihydroxyphthalonitrile and NH_3–EtOH afford 3 : 6-*dihydroxyphthalodiamidine*, decomp. 210—270°.

II. In the formation of (**I**), *o-cyanothiobenzamide* (**III**) and (**II**) are intermediates, generated initially as the NH_4 or alkali salts. The production of (**III**) from *o*-$C_6H_4(CN)_2$ requires the presence of a hydroxylic solvent and is greatly facilitated by the presence of a base (NH_2Ph can take the place of both together). NaSH in EtOH with *o*-$C_6H_4(CN)_2$ gives (**III**), chars at 221—224°, and at room temp. and on boiling the Na_2 salt (+4H_2O) of (**I**) is obtained. This salt is methylated to S-*methyldithio-β-isoindigo*, m.p. 245°, which with EtI affords S-*methyl*-S′-*ethyldithio-β*-iso*indigo*, m.p. 152—153°. NH_2Ph–EtOH and (**II**) yield *thiophthalimidemonophenylimine*, m.p. 209°, and *phthalimidemonophenylimine*, m.p. 161°, is prepared from NH_2Ph and monothiophthalimide. Reduction ($SnCl_2$–HCl) of (**II**) gives *thiophthalimidine*, m.p. 159°. P_2S_5 and phthalimidine afford a *substance*, $C_{16}H_8O_2N_2S$, m.p. >350°, and very little of the thio-compound, which with S at 200° gives (**I**) and H_2S. The following derivatives of (**I**) are prepared by using the appropriate reagent: *thio-β-isoindigomonophenylhydrazone* [S-*Me* derivative, m.p. 220° (decomp.)], *thio-β-isoindigomonophenylimine*, m.p. 265° (S-*Me* derivative, m.p. 212°), and *β-isoindigophenylimine*, m.p. 306°; and from the hydrazone are obtained *β-isoindigo-dibenzylidene-*, m.p. 272°, *-di-p-anisylidene-*, m.p. 259°, and *-tetra-acetyl-dihydrazone*, m.p. 262°. Br and (**I**) give 1-*bromo*-3-*phthalimidyl*iso*indolenine*, m.p. 297°, which with NH_2Ph affords *monoanilo-β-isoindigo*, m.p. 279° (+EtOH, m.p. 280°), and with C_5H_5N yields a *pyridinium bromide* derivative, decomp. ~295° (+H_2O or +3H_2O). *SS′*-Dimethyldithio-*β-iso*indigo and Br give a *dibromide*, m.p. 152—154°, in which the Br may be added on to the double bond. *β-iso*-Indigo and Br in a sealed tube at 100° afford 6 : 6′-*dibromo-β-isoindigo* (?), mixed with other derivatives. Monothiophthalimide with NH_3 does not yield (**I**) but *iminophthalimidine*, m.p. 205°. HCl and (**III**) give a hydrochloride.

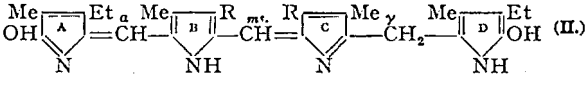
III. *Monothio-β-isoindigo* is obtained from EtOH–NH_3 and H_2S with the residues from the purification of *o*-$C_6H_4(CN)_2$; with NHPh·NH_2 it forms *β-isoindigomonophenylhydrazone*, m.p. 273° (slight decomp.). 1 : 2-$C_{10}H_6(CN)_2$ and EtOH–NH_3–H_2S give 6 : 7 : 6′ : 7′-*dibenzdithio-β-isoindigo*, m.p. >350°, which with MeI affords the SS′-*Me*$_2$ derivative, m.p. 321°. With HCl–EtOH, the Me_2 compound yields the S-*Me* derivative, m.p. >350°, and with H_2SO_4 it forms 6 : 7 : 6′ : 7′-*dibenz-β-isoindigo*, m.p. >350°. 4-Nitrophthalodiamide and Ac_2O give *4-nitrophthalonitrile*, m.p. 142°, reduced and acetylated to the 4-*NHAc*-compound, m.p. 194°, also obtained from 4-*aminophthalodiamide*, m.p. 280—290°. The nitrile with EtOH–NH_3–H_2S affords *diaminodithio-β-isoindigo*. Hot aq. AcOH and other org. acids with the dihydrazone of *β-iso*indigo give a blue *substance*, decomp. ~300°, which is probably a hexahydrated form of a tetrapolymeride of *o*-$C_6H_4(CN)_2$. H_2S and *o*-$C_6H_4(CN)_2$ alone give phthalocyanine. F. R. S.

Preparation of free crystalline biotin. V. Du Vigneaud, K. Hofmann, D. B. Melville, and J. R. Rachele (*J. Biol. Chem.*, 1941, **140**, 763—766; cf. A., 1941, II, 188; III, 896).—Biotin Me ester (**I**) and 0·1N-NaOH at room temp. give free *biotin* (**II**), $C_{10}H_{16}O_3N_2S$, m.p. 230—232° (decomp.), $[\alpha]_D^{22}$ +92° in 0·1N-NaOH, reconverted by CH_2N_2 into (**I**). The titration curve for (**II**) corresponds with that of a monocarboxylic acid. No sp. absorption in the ultra-violet and near ultra-violet region was found. A. T. P.

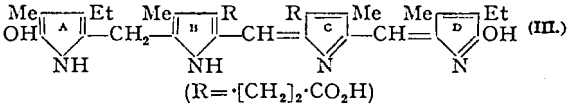
***N*-Glyoxaline derivatives. II.** S. I. Lurie (*J. Gen. Chem. Russ.*, 1940, **10**, 1909—1914).—The Ag salt of benziminazole, shaken with *p*-NHAc·C_6H_4·SO_2Cl (**I**) or *o*-$C_6H_4(CO_2)N$·$[CH_2]_2$·Br (**II**) in EtOH, yields 2-(p-*acetamidobenzenesulphonyl*)*benziminazole* (**III**), m.p. 197—200°, or 2-(*β-phthalimidoethyl*)*benziminazole*, m.p. 214—215°. The Na salt of theophylline and (**I**) or (**II**) in $COMe_2$ yield 7-(p-*acetamidobenzenesulphonyl*)*theophylline* (**IV**), m.p. 200—203°, or 7-(*β-phthalimidoethyl*)*theophylline*, m.p. 255—257°, which when heated under reflux with N_2H_4,HCl in EtOH yields 7-(*β-aminoethyl*)*theophylline* (*dihydrochloride*, m.p. 187—190°). This condenses with (**I**) to 7-[*β*-(p-*acetamidobenzenesulphonamido*)*ethyl*]*theophylline*, m.p. 248—250° (+H_2O, m.p. 159—160°), hydrolysed by 9% HCl in 40% EtOH to 7-[*β*-(p-*aminobenzenesulphonamido*)*ethyl*]*theophylline*, m.p. 250—251°. Lysidine and (**I**) yield 1-(p-*acetamidobenzenesulphonyl*)-2-*methylglyoxaline*, similarly hydrolysed to 1-(p-*aminobenzenesulphonyl*)-2-*methylglyoxaline*, m.p. 228—230°. Hydrolysis of (**III**) or (**IV**) gives sulphanilic acid. R. T.

Dibenziminazoles from dibasic acids. R. L. Shriner and R. W. Upson (*J. Amer. Chem. Soc.*, 1941, **63**, 2277—2278).—*o*-$C_6H_4(NH_2)_2$ (2 mols.) and CO_2H·$[CH_2]_{2-8}$·CO_2H (1 mol.) in 4N-HCl at 125—135° (bath) give 28—63% of 2 : 2′-*ethylene-*, decomp. 325—330° (312—315°), 2 : 2′-*tri-*, decomp. 258—259° (270—273°), *-tetra-*, decomp. 259—260° (305—309°), *-penta-*, decomp. 225—226° (270—272°), *-hexa-*, decomp. 263—266° (296—299°), *-hepta-*, decomp. 273—275° (269—272°), and *-octa-methylene-bisbenziminazole*, decomp. 277—279° (263—265°) (temp. in parentheses are those of decomp. of the *dihydrochlorides*). $H_2C_2O_4$ gives 2 : 3-dihydroxyquinoxaline. $CH_2(CO_2H)_2$ gives 80% of ? a *polyamide*, $C_9H_8O_2N_2$, decomp. 345—349°, insol. in acid. R. S. C.

Mesobiliviolins. I. Constitution of mesobiliviolin; syntheses of mesobiliviolins IXa and XIIIα; ψ-mesobiliviolin and ketourobilin. W. Siedel and H. Möller (*Z. physiol. Chem.*, 1940, **264**, 64—90).—The mesobiliviolin obtained by Fischer *et al.* (A., 1924, i, 1092) from mesobilirubinogen IXa (= urobilinogen) (**I**) and hot aq. HCl–$FeCl_3$ can be separated chromatographically into the violet-red mesobiliviolin IXa (**II**) and the brownish-red mesobilirhodin IXa (**III**), both of which are isomerides of mesobilirubin differing from this in the position of the ·CH_2· bridge. The primary dehydrogenation product



(II.)



(III.)

(R = ·$[CH_2]_2$·CO_2H)

of (**I**) [*i.e.*, the $N_AN_CC_\alpha C_{ms.}$-H_4-derivative of (**II**) = the $N_CN_DC_{ms.}C_\gamma$-H_4-derivative of (**III**)] is urobilin IXα (formed by loss of 2H between $C_{ms.}$ and N_C), which then loses 2 H to give (**II**) and (**III**). *Mesobiliviolin* XIIIα *Me*$_2$ ester [*Me*$_2$ 1′ : 8′-*dihydroxy*-1 : 3 : 6 : 8-*tetramethyl*-2 : 7-*diethyl*-(2′*a*, ms.-5′)-4 : 5-*di-β-propionate*] (**IV**), m.p. 164° (corr.) (*hydrochloride*, m.p. 170°; forms Zn and Cu complex salts), is synthesised from neobilirubic (**V**) and formylneoxanthobilirubic acid (**VI**) in MeOH–48% HBr and N_2. *iso*Neobilirubic acid and (**VI**) similarly give the less stable Me_2 1′ : 8′-dihydroxy-1 : 3 : 6 : 7-tetramethyl-2 : 8-diethyl-(2′*a*, *ms.*-5′)-4 : 5-di-β-propionate [*i.e.*, the Me_2 ester of (**II**)] [hydrochloride, m.p. ~165° (corr.)]. Oxidation of (**I**) with boiling MeOH–25% HCl–$FeCl_3$ also affords the Me_2 ester (hydrochloride, m.p. 150—160°) of (**II**), which is separated chromatographically from other products. Formyl*iso*neoxanthobilirubic acid, (**V**), and MeOH–HBr give the unstable *iso*mesobiliviolin IXα Me_2 ester (**VII**), which changes rapidly (in $CHCl_3$) to a green substance, converted by dil. HNO_3 or HCl into (**III**); the production of (**III**) from (**VII**) probably involves migration of H from N_C to N_B. Reduction of (**IV**) with Na–Hg in aq. MeOH affords mesobilirubinogen XIIIα, m.p. 205°; Zn dust and AcOH yield mesobilirubin XIIIα Me_2 ester [dihydrochloride, m.p. 238·5° (corr.)], whilst H_2–PtO_2–MeOH give dihydromesobilirubin XIIIα Me_2 ester (oxidised by air to the mesobilirhodin). Reduction (Na–Hg) of bilirubin or the Me_2 ester of (**II**) affords the less stable mesobilirubinogen IXα, m.p. 200—205° or 195—200° (mixed m.p. 195—202°), which is readily oxidised (air) to urobilin. The "mesobiliviolinogen" of Fischer *et al.* (*loc. cit.*) is thus a mesobilirubinogen. Oxidation [$Pb(OAc)_4$–AcOH at 60° or Br–$CHCl_3$ on Zn complex salt] of (**IV**) gives ketourobilin XIIIα Me_2 ester (probably contains C_α:O), which is dehydrogenated by MeOH–25% HCl–$FeCl_3$ to (probably) ketomesobilirhodin XIIIα. Glaucobilin Me_2 ester is formed from (**IV**) and excess of $FeCl_3$ in MeOH–25% HCl. When kept for some time (**IV**) partly isomerises to *ψ*-mesobiliviolin XIIIα Me_2 ester (separated chromatographically), which behaves as (**IV**) towards Na–Hg, Zn–AcOH, or $Pb(OAc)_4$ but is degraded by $FeCl_3$ to colourless substances. Debye–Scherrer diagrams of the various bilirubinoids are appended. H. B.

Porphyrins. XLIV. Conversion of hæmin into deuteroporphyrin-2 : 4-dicarboxylic acid tetramethyl ester and of hæmatoporphyrin into diacetyldeuteroporphyrin. H. Fischer and K. O. Deilmann (*Annalen*, 1940, **545**, 22—27).—Oxidation of hæmin (1 g.) with $KMnO_4$ in aq. C_5H_5N at room temp. (shaking for 42 hr.), removal of Fe from the residue

obtained after evaporation in a vac. by $Fe(OAc)_2$–HCl, subsequent fractionation with Et_2O and aq. HCl, and final esterification (CH_2N_2) gives *deuteroporphyrin-2 : 4-dicarboxylic acid Me*$_4$ ester (30—35 mg.), m.p. 185° (*Zn* salt, m.p. 274—280°). Similar oxidation of protoporphyrin affords a small amount of a cryst. substance which forms an oxime. Hæmatoporphyrin is oxidised by $Na_2Cr_2O_7$ in C_5H_5N at 100° (bath) to diacetyldeuteroporphyrin (13%) (Me_2 ester, m.p. 239°). H. B.

Morpholine derivatives.—See B., 1941, II, 407.

Thiazolinyl sulphides.—See B., 1941, II, 335.

Preparation of phenthiazine. E. P. Belokvinitzki (*J. Appl. Chem. Russ.*, 1941, **14**, 187—191).—Phenthiazine is obtained in theoretical yield by heating a mixture of $NHPh_2$ 100, S 38, and I 0·5 g. for 10—15 min. at 190—200° (cf. A., 1914, i, 519). R. T.

4-Thienyl-2-methylthiazole.—See B., 1941, II, 374.

Vitamin-B_1. XX. Analogues of aneurin. Their physiological activity. G. A. Stein, W. L. Sampson. J. K. Cline, and J. R. Stevens (*J. Amer. Chem. Soc.*, 1941, **63**, 2059—2062; cf. A., 1940, II, 285).—$CHO{\cdot}CNa(CH_2{\cdot}OEt){\cdot}CO_2Et$, prepared *in situ* from $OEt{\cdot}[CH_2]_2{\cdot}CO_2Et$, HCO_2Et, and Na in light petroleum at 30—35°, is treated with $NH_2{\cdot}CEt{:}NH_2$,HCl in H_2O at −5° and then with NaOH and kept at 0°. *4-Hydroxy-2-ethyl-5-ethoxymethylpyrimidine*, m.p. 146—146·5°, sublimes at 120°/0·5 mm., thus obtained (55%), with $POCl_3$ at 80° gives the 4-Cl-compound, which with NH_3–EtOH at 120° yields *4-amino-2-ethyl-5-ethoxymethylpyrimidine*, m.p. 64·5—65·5°. This is converted by HBr–AcOH at 100° into the 5-CH_2Br compound hydrobromide, m.p. 175—178°, which with 4-methyl-5-β-hydroxyethylthiazole (**I**) in light petroleum gives 4-methyl-5-β-hydroxyethyl-5′-4′-amino-2′-ethylpyrimidylmethylthiazolinium bromide hydrobromide (**II**), m.p. 235·5—236° (decomp.). 4-Hydroxy-2-methyl-6-ethoxymethylpyrimidine, m.p. 158°, and $POCl_3$ at 80° give oily 4-chloro- and thence (NH_3–MeOH; 125°) *4-amino-2-methyl-6-ethoxymethylpyrimidine*, m.p. 95·5—96°, which could not be converted into the $CH_2{\cdot}OH$ compound. *4-Hydroxy-5-methyl-6-ethoxymethylpyrimidine* (prep. from its 2-SH derivative by 8% H_2O_2 at 75—80°), m.p. 118°, is similarly converted into the 4-NH_2-compound, m.p. 137—138°, whence HBr–AcOH at 80° gives 4-amino-5-methyl-6-bromomethylpyrimidine hydrobromide. With (**I**) at 115—120° this gives *4-methyl-5-β-hydroxyethyl-6′-4′-amino-5′-methylpyrimidylmethylthiazolinium bromide hydrobromide* (**III**), m.p. 233—234° (decomp.). In vitamin-B_1 activity (prophylactic and curative) (**II**) equals aneurin, but (**III**), 4-methyl-5-β-hydroxyethyl-5′-4′-amino-6′-methyl- and -6′-4′-amino-2′-methyl-pyrimidylmethylthiazolinium bromide hydrobromide are inactive (cf. lit.). R. S. C.

Thiazyl sulphides.—See B., 1941, II, 374, 404.

Alkaloidal substance from *Carica papaya* seeds. T. B. Panse and A. S. Paranjpe (*Rasāyanam*, 1941, **1**, 215—216).—Extraction of the dried seeds with Prollius' fluid leads to an oil and *carpasemine* (**I**), $C_8H_{10}O_2N_2$, m.p. 165° (*Ac*, m.p. 132°, and *Bz*, m.p. 125°, derivatives). (**I**) is a weak base, neutral to litmus. It gives positive tests with the usual alkaloidal reagents and forms an additive compound with $PtCl_4$. H. W.

Cinchona alkaloids in pneumonia. IX. Quaternary salts. (Miss) M. A. Clapp, (Miss) A. G. Renfrew, and L. H. Cretcher (*J. Amer. Chem. Soc.*, 1941, **63**, 2169—2171; cf. A., 1941, II, 79).—Interaction of β-hydroxyethyl*apo*cupreine with $CH_2Cl{\cdot}CO{\cdot}NHAr$ in boiling, dry $COMe_2$ gives *β-hydroxyethyl-apocupreinium carbo-β-*p*-hydroxyethylanilido-*, $[\alpha]_D^{26}$ −59·4° in H_2O, *carbo-*p*-hydroxyanilido-*, $[\alpha]_D$ −87·6° in H_2O, and *carbanilido-*, $[\alpha]_D$ −89·2° in H_2O, *-methochloride hydrochloride*, which have very low antipneumococcic activity. *Cinchonidinium carbo-*p*-hydroxyanilidomethochloride*, $[\alpha]_D^{21}$ −30·3±0·5° in C_5H_5N (*hydrochloride*, $[\alpha]_D^{21}$ −47·0° in H_2O), also has very slight activity. R. S. C.

***Aconitum* alkaloids. XIV. Formation of ketones from *Aconitum* alkaloids.** R. Majima and K. Tamura (*Annalen*, 1940, **545**, 1—21).—Mesaconitine (Morio, A., 1930, 228) and aq. CrO_3 in cold $COMe_2$ for 10 days give ~80% of *mesaconitinone* (**I**), $C_{33}H_{43}O_{11}N$, decomp. 173°, $[\alpha]_D^{20}$ −35° in $CHCl_3$ [*semicarbazone*, decomp. 214°; *aurichloride*, decomp. 226°; *perchlorate*, decomp. 215°; *Ac*$_2$ derivative, decomp. 215°, prepared by AcCl at 35° (sealed tube)/5 days, readily oxidised by $KMnO_4$ to non-cryst. products], which contains 2·7—2·8 active H (excess over 2 probably due to an enolic OH). Boiling dil. H_2SO_4 (1 equiv.) hydrolyses (**I**) to AcOH (1 equiv.) and benzmesaconinone, $C_{31}H_{41}O_{10}N$ [*hydrochloride* (+$4H_2O$), m.p. ~230° (decomp. ~221°)]. At 175°/15 mm. in H_2, (**I**) loses 1 mol. each of MeOH and H_2O to give the alkali-insol. *demethanolanhydromesaconitinone* (**II**), $C_{32}H_{37}O_9N$, m.p. 194—194·5°, $[\alpha]_D^{20}$ +26·24° in $CHCl_3$ [*Ac*$_2$ derivative (**III**), decomp. 157°], which contains 2 active H, does not react with CH_2N_2, decolorises Br slowly, and does not give Liebermann's reaction. At 219° (**II**) loses 1 mol. of AcOH and yields a little of a *substance*, decomp. 252°. Dissolution of (**II**) in dil. HCl and pptn. with aq. NH_3 affords *demethanolmesaconitinone*, $C_{32}H_{39}O_{10}N$ (*hydrobromide*, decomp. 212°; *perchlorate*, decomp. 226°; *picrate*, decomp. 194°), which loses H_2O only at high temp./vac. over P_2O_5. Hydrolysis of (**II**) with dil. H_2SO_4 gives *benzdemethanolmesaconinone*, $C_{30}H_{37}O_9N$, decomp. 247—249°, whilst with boiling aq. EtOH–KOH *demethanolmesaconinone*, $C_{23}H_{33}O_8N$, decomp. 250—252°, $[\alpha]_D^{21}$ +76·5° in H_2O [*hydrochloride* (+H_2O), decomp. 267°], results. Reduction (H_2, Pd, EtOH) of (**III**) affords *dihydrodiacetyldemethanolmesaconitinone*, $C_{36}H_{45}O_{12}N$, m.p. ~204°, $[\alpha]_D^{30}$ −31·2° in $CHCl_3$, hydrolysed (aq. EtOH–KOH) to *dihydrodemethanolmesaconinone*, $C_{23}H_{35}O_8N$, decomp. 263°, which is reduced (H_2, PtO_2, AcOH) to tetrahydrodemethanolmesaconinone (*hydrochloride*, decomp. 235°). An aromatic nucleus is not present in (**II**). Oxidation (CrO_3, AcOH) of aconitine gives aconitinone (**IV**), $C_{30}H_{33}O_7N(OMe)_4$, m.p. ~150° (decomp.) (rapid heating), resolidifying with m.p. 212° (decomp.) [*perchlorate*, decomp. 197° (sinters ~185°)], and not aconitolone (Lawson, A., 1936, 351). Loss of MeOH from (**IV**) occurs gradually at room temp. and rapidly when heated, yielding *demethanolaconitinone* (**V**), $C_{33}H_{41}O_{10}N$, m.p. 220° (decomp.), $[\alpha]_D^{20}$ +69·28° in $CHCl_3$ [also isolable from the mother-liquor after crystallisation of (**IV**) from MeOH; *aurichloride*, m.p. ~177°; *picrate*, decomp. 197—198°], which is hydrolysed (aq. EtOH–KOH) to demethanolaconinone, $C_{24}H_{35}O_8N$ [*hydrochloride* (+$3H_2O$), decomp. 224°]. At 219° (**V**) loses AcOH and passes into pyrodemethanolaconitinone, $C_{31}H_{37}O_8N$, amorphous, m.p. 115—130° [*aurichloride*, decomp. 196°; *perchlorate* (+ H_2O) (**VI**), decomp. 257°; *hydrochloride*, decomp. 224°; the base recovered from the EtOH mother-liquor of (**VI**) affords a *hydrochloride*, decomp. 196° (sinters ~189°)]. Oxidation of (**II**) or (**V**) with HNO_3 (*d* 1·43) in AcOH at 80° gives nitronitrosoaconitic acid (**VII**), $C_{28}H_{34}O_{10}N_3(OMe)_3$,EtOH,$H_2O$, softens 180°, decomp. 282°, $[\alpha]_D^{14\,(15)}$ −31·94° (−33·92°) in EtOAc (cf. Suginone, A., 1938, II, 74). Hypaconitine (A., 1930, 228) is largely unaffected by CrO_3 or HNO_3, whilst hypoxonitine and conc. HNO_3 afford a non-cryst. product. *iso*-$C_5H_{11}{\cdot}O{\cdot}NO$ and (**I**) in AcOH–HCl give *oximinomesaconitinone*, decomp. 236°, $[\alpha]_D^{30\cdot5}$ −98·9° in $CHCl_3$ (*aurichloride* and *picrate*, both soften at 203° and then gradually blacken), oxidised (N_2O_3 in cold $CHCl_3$) to the nitrite, decomp. 205°, of *nitromesaconitinone* (**VIII**), m.p. 215° (sinters ~161°; decomp. 175°), $[\alpha]_D^{30\cdot5}$ −41·4° in $CHCl_3$ (hydrochloride, decomp. 181°). Oxidation (HNO_3) of (**VIII**) affords (**VII**). Mesaconitine probably contains the group ·$CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}C(OMe){\cdot}CH_2{\cdot}NMe$· in addition to 2 OH, OMe, OAc, and OBz. H. B.

***Strychnos* alkaloids. XXII. Degradation of quaternary salts of the vomicine group.** H. Wieland and O. Müller. **XXIII. Vomicine.** H. Wieland and O. Schmauss. **XXIV. Oxidation of derivatives of vomicidine.** H. Wieland and R. G. Jennen (*Annalen*, 1940, **545**, 59—71, 72—85, 86—98).—XXII. Vomicine (**I**) and Me_2SO_4 in boiling C_6H_6 (pure, dry reagents must be used under strictly anhyd. conditions) give (cf. A., 1929, 708) the quaternary *methosulphate* (+$2H_2O$; crystallisation from H_2O) (**II**), m.p. 272° (decomp.), whence *methylvomicinium iodide* (+$2H_2O$), m.p. ~220°, bromide, m.p. 221°, chloride, m.p. 265° (decomp.), and perchlorate, decomp. ~315°, are obtained. Electrolytic reduction (Pb cathode) of (**II**) in 40% H_2SO_4, removal of H_2SO_4 with $Ba(OH)_2$, and subsequent treatment with KI gives methylvomicidinium iodide, m.p. >300° [corresponding perchlorate, m.p. 280° (decomp.)]. The quaternary hydroxide from (**II**) and $Ba(OH)_2$ or from the halides and TlOH (not Ag_2O owing to its reduction) is unstable and isomerises to *vomicinemethylbetaine* (**III**), $C_{23}H_{28}O_5N_2$ (+$3H_2O$), m.p. 224°, which does not add MeI and is reduced (H_2, PtO_2, H_2O) to a H_2-derivative, m.p. 260° (decomp.). Solutions of (**III**) in aq. NaOH are sensitive to air, but a Na salt can be obtained by evaporation in a vac. Concn. of a solution of (**III**) in aq. HBr at low

temp. gives the hydrobromide, decomp. ~300° [with aq. Na_2CO_3 affords (**III**)], solutions of which slowly (more rapidly when heated) pass into those of the quaternary salt. Dihydrovomicine (**IV**) and MeI at 100° (sealed tube) afford the methiodide, m.p. 261°; the methosulphate [prep. as for (**II**)] with Na–Hg in warm 0·5N-AcOH regenerates (**IV**). Catalytic reduction (PtO_2) of the quaternary salts of (**I**) gives those of (**IV**). Reduction of (**II**) with 5% Na–Hg in N-AcOH + N-NaOAc at 60—70° yields 30—40% of "*methylvomicine*" (**V**), $C_{23}H_{28}O_4N_2$, m.p. 236·5° [hydrochloride, m.p. 308° (decomp.); perchlorate, decomp. >300°], which contains OMe and NMe, and is reduced (H_2, PtO_2, 2N-AcOH) to a H_4-derivative [*picrate*, m.p. 220° (decomp.)]. Demethylation [AcOH–HI (*d* 1·7) and red P; aq. HBr] of (**V**) gives an impure *base*, $C_{22}H_{26}O_4N_2$, m.p. 294°. The methiodide, m.p. 244—245° (decomp.) (formed readily in the cold), of (**V**) is reduced (Na–Hg, aq. AcOH–NaOAc) to "*dimethylvomicine*" (**VI**), $C_{24}H_{32}O_4N_2$, m.p. 114° [obtained cryst. through the perchlorate, m.p. 274° (decomp.)], further reduced (H_2, PtO_2, 2N-AcOH) to a H_2-derivative, m.p. 139°. The methiodide, m.p. 261°, of (**VI**) is unaffected by Na–Hg or boiling aq. NaOH; the quaternary hydroxide (prep. by Ag_2O) decomposes at 160° to NMe_3 and a non-cryst. substance. Deoxyvomicine methobromide is reduced (Na–Hg) to a *base* (**VII**), $C_{23}H_{30}O_3N_2$, m.p. 221°, $[\alpha]_D$ +99·6° in $CHCl_3$, which contains 2 NMe but no OMe; the *methiodide*, m.p. 248° (decomp.), of (**VII**) with Ag_2O in cold H_2O (reduction occurs if warmed) gives the hydroxide (loses NMe_3 at 150°). Reduction (H_2, PtO_2, 2N-AcOH) of (**VII**) affords a 3 : 1 mixture of isomeric H_4-derivatives, m.p. 150° and 214°.

XXIII. Deoxyvomicidine (**VIII**) [*methiodide* (+$2H_2O$), m.p. 175°, obtained in poor yield] is prepared *in situ* by electrolytic reduction (Pb electrodes) of colourless deoxyvomicine (**IX**), m.p. 207°, $[\alpha]_D^{20}$ +209° in $CHCl_3$ [*methiodide*, m.p. 270° (decomp.)], in dil. H_2SO_4, and then oxidised (CrO_3) at 0°—room temp. to a *base*, $C_{16}H_{20}ON_2$, m.p. 70°, $[\alpha]_D^{20}$ +341° in $CHCl_3$ [*dihydrochloride* (+H_2O) (**X**), m.p. 256° (decomp.); perchlorate, m.p. 263° (decomp.)]. Reduction (H_2, PtO_2, H_2O) of (**X**) gives a base, $C_{16}H_{24}N_2$ (*methiodide*, m.p. 178°), whilst (**VIII**) (in AcOH) affords a base, $C_{22}H_{30}ON_2$ [*hydrochloride* (+0·5EtOH), m.p. 250—254° (decomp.)]. Vomicine with AcOH–HI (*d* 1·96) and red P yields (cf. A., 1929, 708) (**IX**) and a small amount of an I-containing base, decomp. 225°, which with Zn dust and AcOH affords a *dihydrodeoxyvomicine*, m.p. 194°, $[\alpha]_D^{20}$ +173° in $CHCl_3$; the primary product of the HI reduction is not (**IX**) but the yellow modification (**XI**), new m.p. 211°, $[\alpha]_D^{22}$ +242° in $CHCl_3$ (cf. A., 1937, II, 126), which when heated for a long time with $CHCl_3$ (used for extraction of the crude reduction product) or EtOH passes into (**IX**). The absorption spectra of (**IX**) and (**XI**) are different. Furthermore, (**IX**) absorbs ~8 H on catalytic reduction (PtO_2, AcOH) to give two *bases*, $C_{22}H_{30}O_2N_2$, m.p. 177°, $[\alpha]_D^{21}$ −94·4° in $CHCl_3$, and m.p. 143° (may not be pure), in addition to the isomeride, m.p. 211°, $[\alpha]_D^{21}$ +73° in $CHCl_3$, previously described (A., 1933, 1312); (**XI**) similarly slowly absorbs 4 H forming the base, $C_{22}H_{28}O_3N_2$, m.p. 220° (*loc. cit.*), which may also be produced from (**IV**). The acid, $C_{17}H_{22}O_7N_2$ (A., 1929, 708), is now shown to be $C_{16}H_{20}O_6N_2$ (+$5H_2O$); with CH_2N_2 it gives a *compound*, $C_{18}H_{24}O_6N_2$, and it is decarboxylated at 200° to a *base*, $C_{15}H_{20}O_4N_2$, m.p. 264—266°, $[\alpha]_D^{18}$ −51·3° in $CHCl_3$, which contains NMe (does not add MeI) and 1 active H, and does not give the CHI_3 reaction.

XXIV. Electrolytic reduction (Pb electrodes) of dihydrodeoxyvomicine in 60% H_2SO_4 and subsequent neutralisation (conc. aq. NH_3 at >5°) gives the unstable *dihydrodeoxyvomicidine*, decomp. 264° (darkens from 240°) [*methiodide* (+$3H_2O$), m.p. 204° (decomp.)], which is oxidised (CrO_3, aq. H_2SO_4) to a *base*, $C_{16}H_{22}ON_2$, m.p. 88° [*dihydrochloride* (+H_2O) (**XII**), m.p. 255° (decomp.); in some cases an anhyd. *dihydrochloride*, m.p. 282°, is obtained]. With Pd at 220°, (**XII**) affords a NMe-free base, $C_{15}H_{20}N_2$ (as *dihydrochloride*, decomp. 300°). Oxidation (CrO_3, dil. H_2SO_4) of dihydrovomicidine (prep. *in situ* by electrolytic reduction of dihydrovomicine in 60% H_2SO_4) gives a poor yield of an *acid*, $C_{16}H_{20}O_4N_2,3H_2O$, decomp. 264° (darkens from 220°) (*hydrochloride*, decomp. >300°; Me_1 ester *dihydrochloride*, decomp. 286°). Electrolytic reduction of *iso*dihydrovomicine affords *iso*dihydrodeoxyvomicidine (*dihydrochloride*, decomp. ~215°), oxidised (CrO_3 ≡ 30 O; dil. H_2SO_4) to a base, $C_{16}H_{20}O_3N_2$ (*dihydrochloride*, decomp. 295°, absorbs 4 H on catalytic reduction). Partial structures are suggested for many of the compounds. H. B.

VI.—ORGANO-METALLIC COMPOUNDS.

Arsinoanilinotriazines.—See B., 1941, III, 270.

Preparation of *p*-aminobenzenephosphonic [phosphanilic] acid. H. Bauer (*J. Amer. Chem. Soc.*, 1941, **63**, 2137—2138). —*p*-$C_6H_4Cl{\cdot}PO_3H_2$ (modified prep.), m.p. 188° (lit. 184—185°) (NH_4 salt), and freshly prepared Cu_2O (1 mol.) in 28% aq. NH_3 at 150° give 62% (Cu gives only 5—15%) of *phosphanilic acid*, m.p. 245° (decomp.), resolidifies, remelts at ~285° [*Ac* derivative, m.p. 229° (decomp.)]. R. S. C.

Thiophen series. LIV. Mercuration of nitrated thiophens. W. Steinkopf (*Annalen*, 1940, **545**, 38—45).—3-Nitrothiophen (**I**) (1 g.) and HgO (6 g.) in boiling AcOH (50 c.c.) for 1 hr. give the *tri*(*acetoxymercuri*)-derivative (**II**), amorphous, darkens >270°, converted by aq. KI–I into 2 : 4 : 5-*tri-iodo*-3-*nitrothiophen* (**III**), m.p. 169·5—170·5°. $Hg(OAc)_2$ (4 g.) and (**I**) (1 g.) in 50% AcOH (40 c.c.) first at 55—60° (30 min.) and then at 95° (1 hr.) afford the 2 : 5-*di*(*acetoxymercuri*)-derivative, decomp. ~220° (preheated bath), and thence 2 : 5-*di-iodo*-3-*nitrothiophen*, m.p. 108·5—110°. The product obtained from a nitrothiophen, m.p. 42—43° [mixture of (**I**) and 2-nitrothiophen (**IV**) obtained by nitration of thiophen], and HgO in boiling AcOH is converted into (**III**) and 2 : 3-*di-iodo*-5-*nitrothiophen* (**V**), m.p. 98—99°. The compound, m.p. 79—80°, obtained by nitration of 2 : 3-di-iodothiophen and previously described (A., 1937, II, 163) as (**V**), is now shown to be a mixture of impure (**V**) and 3-*iodo*-2-*nitrothiophen*, m.p. 131—134°. Nitro-2-thiophenic acid, m.p. 130—135° (Römer, A., 1887, 362), and HgO in boiling AcOH give mainly (**II**) [and thence by distillation with dil. HCl pure (**I**), m.p. 78—79° (lit. 67—69°, 75—77°); this method is recommended for the prep. of small amounts of (**I**)]; the product from the mother-liquors similarly affords a mixture of (**I**) and (**IV**). 5-Nitro-2 : 2′-dithienyl and $Hg(OAc)_2$ in AcOH at 100° (bath) give the 3 : 3′ : 5′-*tri*(*acetoxymercuri*)-derivative, yellow, becomes orange-red and amorphous at 140°, converted by boiling H_2O into the red 3 : 3′-*di*(*hydroxymercuri*)-5′-*acetoxymercuri*-derivative and by aq. KI–I into 3 : 3′ : 5′-*tri-iodo*-5-*nitro*-2 : 2′-*dithienyl*, m.p. 187—189°. H. B.

Thiophen series. LV. 2-Methyl-3-ethyl- and 3-methyl-2-ethyl-thiophen and derivatives. W. Steinkopf, A. Merckoll, and H. Strauch (*Annalen*, 1940, **545**, 45—51).—Et_2 α-*acetyl*-α-*ethylsuccinate*, b.p. 143—145°/14 mm. (from Et_2 sodioacetosuccinate and EtI in boiling C_6H_6), is hydrolysed (dil. HCl) to β-*ethyl-lævulic acid*, b.p. 144—146°/14 mm., which with P_2S_5 at 130—140° gives 2-*methyl*-3-*ethylthiophen* (**I**), b.p. 156—157°. With $HgCl_2$ and NaOAc in aq. EtOH, (**I**) affords the 5-*ClHg*-derivative (**II**), m.p. 150—151°, converted by NaI (2 mols.) in $COMe_2$ into *Hg di*-2-*methyl*-3-*ethyl*-5-*thienyl*, m.p. 85—85·5°, which with $HgHal_2$ in $COMe_2$ gives 5-*bromomercuri*-, m.p. 165·5—166·5°, and 5-*iodomercuri*-2-*methyl*-3-*ethylthiophen*, m.p. 157·5—158°. 2-*Methyl*-3-*ethyl*-5-*acetothienone*, b.p. 132—134°/16 mm. (p-*nitrophenylhydrazone*, m.p. 189·5°), is obtained from (**I**), AcCl, and $AlCl_3$ in light petroleum. 5-*Iodo*-2-*methyl*-3-*ethylthiophen*, b.p. 103—103·5°/4 mm. [from (**II**) and aq. NaI–I], with Cu-bronze at 210—225° affords 5 : 5′-*dimethyl*-4 : 4′-*diethyl*-2 : 2′-*dithienyl*, m.p. 48·8—49·4° [3 : 3′-*di*(*acetoxymercuri*)-derivative, decomp. 225—230°]. Clemmensen reduction of 3-methyl-2-acetothienone gives 3-*methyl*-2-*ethylthiophen* (**III**), b.p. 160—161·5° (5-*ClHg*-derivative, m.p. 172—173° after sintering, converted by NaI in $COMe_2$ into the 5-*IHg*-derivative, m.p. 156—157°, and *Hg di*-3-*methyl*-2-*ethyl*-5-*thienyl*, m.p. 99—100°). Excess of aq. $Hg(OAc)_2$ converts (**III**) into the 4 : 5-*di*(*acetoxymercuri*)-derivative, m.p. 248—250° (decomp.). 3-*Methyl*-2-*ethyl*-5-*acetothienone*, b.p. 140—143·5°/14 mm. [p-*nitrophenylhydrazone*, m.p. 186—187°; *semicarbazone*, m.p. 228·5—229° (decomp.)], is prepared. H. B.

Phenyl- and 3-pyridyl-mercuri salts.—See B., 1941, III, 270.

Relative reactivities of organo-metallic compounds. XXXIX. Addition reactions of organo-metallic compounds with conjugated systems. H. Gilman and R. H. Kirby (*J. Amer. Chem. Soc.*, 1941, **63**, 2046—2048; cf. A., 1941, II, 273).—1 : 4-Addition to COPh·CH:CHPh (**I**) occurs with the less reactive $BePh_2$, $ZnPh_2$, $AlPh_3$, and MnPhI, and 1 : 2-addition with more reactive CaPhI, KPh, LiPh, and NaPh. LiPh gives 13% of $CHPh_2{\cdot}CH_2{\cdot}COPh$ as well as, mainly, CHPh:CH·CPh_2·OH (cf. lit.). Similarly, with *p*-$NMe_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COPh$ (**II**), MgPhBr and $BePh_2$ give *p*-

$NMe_2·C_6H_4·CHPh·CH_2·COPh$ (**III**) (66 and 71%, respectively) (cf. lit.), CaPhI gives *diphenyl-p-dimethylaminostyrylcarbinol* (**IV**), m.p. 117° (64%), and LiPh gives (**III**) 14 and (**IV**) 76%. CPh_2:NPh with NaPh or KPh gives $CPh_3·NHPh$ by 1 : 2-addition. Interaction with (**I**) is used to show the interconversions, $BeCl_2 + 2LiPh \rightarrow BePh_2 + 2LiCl$, $MnI_2 + LiPh \rightarrow MnPhI + LiI$, and $MgI_2 + p\text{-}NMe_2·C_6H_4Li \rightarrow LiI + p\text{-}NMe_2·C_6H_4·MgI$. *p*-$NMe_2·C_6H_4·MgI$ with (**I**) gives (**III**). *p*-$NMe_2·C_6H_4Li$ with (**I**) gives *phenyl-p-dimethylaminophenylstyrylcarbinol* (75%), m.p. 131°, and (**III**) (12%). R. S. C.

VIII.—ANALYSIS.

Rapid preliminary determination of m.p.—See A., 1941, **I**, 484.

Advances in microchemistry. I. Quantitative organic micro-analysis. H. Roth (*Angew. Chem.*, 1940, **53**, 441—450).—Recent work (145 references) on micro-balances and on the following determinations is summarised briefly: C, H, O, N, halogens, S, P, As, metals in org. compounds, equiv. wt., active H; the CO, OMe, OEt, NHAlk, OAc, and CMe_2 groups and double linkings; the sap., I, and diene vals.; and of mol. wt. by the b.p. elevation, f.p. depression, osmotic pressure, and v.p. methods. J. G.

Systematic qualitative organic micro-analysis. Improved apparatus for micro-preparative work. H. K. Alber (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 656—658).—The construction and operation of the following are described: an improved balance for micro-preparative work, sensitive to 0·1 mg., based on the Friedrich torsion spring micro-balance; a micro-mortar and pestle for grinding small quantities of material (data are presented on recoveries of materials of varying hardness); a combined separatory and sedimentation funnel, which has a small sediment collector in the stopcock. J. D. R.

Removal of nitrogen oxides in semi-micro-determination of carbon and hydrogen. P. J. Elving and W. R. McElroy (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 660—663).—The defects in the use of PbO_2 in org. combustions are discussed, and suggested substitutes are described. Various metals and oxides remove N oxides satisfactorily but are excluded as they give low C and H vals. The use of a solution of $KMnO_4$ in H_2SO_4 between the H_2O and CO_2 absorption tubes gives improved results, and is considered to be better and cheaper than PbO_2; this also simplifies the tube filling. J. D. R.

Report on recommended specifications for microchemical apparatus. Carbon–hydrogen and Dumas nitrogen. G. L. Royer, H. K. Alber, L. T. Hallett, W. F. Spikes, and J. A. Kuck (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 574—580).—Specifications for various units for the C–H and Dumas N determinations by the Pregl technique are illustrated fully. L. S. T.

Modifications in the combustion micro-method for carbon and hydrogen. G. L. Royer, A. R. Norton, and O. E. Sundberg (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 688—690).—A detailed description is given of an automatic combustion furnace controlled by time switches, and of modifications in the H_2O and CO_2 absorption tube assembly which adapt the normal C and H determination apparatus to the new automatic furnace. The use of one-rate automatic combustion, ground-glass joints for connecting the absorption tubes, weighing the tubes filled with O_2, simplification of filling, elimination of preheater, and shorter intervals for the weighing of the absorption tubes make the procedure applicable to routine industrial analysis. J. D. R.

Effect on selenium on the Kjeldahl digestion. R. B. Bradstreet (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 657).—In the Kjeldahl determination of N, the use of Se catalyst, alone or with $FeSO_4$ or $CuSO_4$, causes a loss of N, and quantities >0·25 g. should not be used. J. D. R.

Micro-Kjeldahl determination of nitrogen. E. P. Clark (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 641—647).—Apparatus (digester; Parnas–Wagner type still) and standard procedure are recommended. The sample is weighed on tared cigarette paper, which is digested with the sample, Hg is removed by addition of $Na_2S_2O_3$ with the alkali, and the NH_3 is collected in 4% aq. H_3BO_3 and titrated (Me-red) with 0·02N-HCl. By using Friedrich's modification (A., 1933, 621) N in compounds containing N·N, NO, and NO_2 groups may be determined with precision. A. A. E.

Micro- and semi-micro-Kjeldahl method for the determination of nitrogen. F. Acree, jun. (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 648—651).—Satisfactory results were obtained by using Clark's procedure (preceding abstract) for the determination of N in 15 compounds, employing 5—20-mg. samples. A. A. E.

Direct determination of oxygen in organic compounds by hydrogenation. III. Reduction mechanism on the nickel–thoria catalyst. K. Morikawa, T. Kimoto, and R. Abe (*Bull. Chem. Soc. Japan*, 1941, **16**, 229—232; cf. A., 1941, II, 157).—$CO + CO_2$ produced in the cracking zone at 950° are reduced on the Ni–ThO_2 catalyst in H_2 at 350°; relations between temp. and equilibrium consts. of the reactions $CO + 3H_2 = CH_4 + H_2O$ and $CO_2 + 4H_2 = CH_4 + 2H_2O$ are discussed. Sucrose, cellulose, lignin, and brown coal of Jarahinohl mine (Manchoukuo) are decomposed at various temp. in H_2 and % O evolved as volatile O compound is measured; little change resulted from varying the time of reaction between 10 and 30 min. Classification of O bonds in the samples is recorded; *e.g.*, sucrose affords 72·73% of alcoholic O, 18·18% of pyran- or furan-O, and 9·09% of etheric O, of the total O (51·43%). A. T. P.

Analytical investigation of hydrocarbon mixtures by means of Raman spectra. Detection of paraffins and olefines with straight and branched chains. J. Goubeau and (Frl.) V. von Schneider (*Angew Chem.*, 1940, **53**, 531—535).—The method previously described (cf. A., 1938, II, 120) has been applied to the analysis of 12 hydrocarbon fractions. The data are presented in detail and include a table comparing the Raman frequencies of the fractions with those of 18 pure hydrocarbons. C. R. H.

Determination of alcohols in dilute aqueous solution. R. Skrabal (*Z. anal. Chem.*, 1940, **119**, 222—226).—Modifications of and improvements in the Fischer–Schmidt method (A., 1926, 632) are described. It can then be extended to unsaturated alcohols. Cylinder N_2, freed from O_2, replaces CO_2, and the absorption flasks are fitted with sintered-glass discs to facilitate absorption. Details of procedure, and data for PrOH and allyl alcohol, are given. L. S. T.

Distinction and identification of *n*- and *iso*-propyl alcohol with mercuric sulphate. G. Denigès (*Bull. Trav. Soc. Pharm. Bordeaux*, 1938, **76**, 72—77; *Chem. Zentr.*, 1938, ii, 3960).—On warming, $HgSO_4$ solution and Pr$^\beta$OH give a white ppt. (spherical and radial aggregates under the microscope), which turns brown on addition of NH_3. Under similar conditions Pr$^\alpha$OH gives pale yellow needle crystals in 4—5 min. Addition of 2—3 drops of Br before warming accelerates and inhibits pptn. with Pr$^\beta$OH and Pr$^\alpha$OH, respectively. A. J. E. W.

Potentiometric determination of mercaptans in aqueous alkaline solution. M. W. Tamele, L. B. Ryland, and V. C. Irvine (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 618—622).—The mercaptan in N-NaOH—0·05N-aq. NH_3 is titrated with standard $AgNO_3$ with a Ag electrode, and the e.m.f. of the cell formed by this solution in contact with a standard reference electrode (*e.g.*, Hg–0·1N-NaOAc) is plotted against ml. of $AgNO_3$. The method is sp. for mercaptans; usual impurities accompanying these in petroleum products do not interfere. J. D. R.

Cerate oxidimetry. Determination of glycerol. G. F. Smith and F. R. Duke (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 558—560).—The procedure detailed depends on the reaction $C_3H_8O_3 + 8H_2Ce(ClO_4)_6 + 3H_2O = 3HCO_2H + 8Ce(ClO_4)_3 + 24HClO_4$. The excess of $H_2Ce(ClO_4)_6$ is determined by titration with $Na_2C_2O_4$ (nitro-*o*-phenanthroline). A potentiometric end-point is thus avoided. Other advantages over the $K_2Cr_2O_7$–$FeSO_4$ method are that the time required for oxidation of the glycerol (**I**) is reduced from 180 to 15 min., and the reaction temp. from 90—100° to 50—60°. Oxidation of (**I**) can also be effected by means of $(NH_4)_2Ce(SO_4)_4.2H_2O$ in 0·5M-H_2SO_4. The two methods compare favourably with existing procedures. L. S. T.

Determination of α-glycerophosphates in aqueous solution by lead tetra-acetate. D. J. Wormith and J. J. Rae (*J. Amer. Chem. Soc.*, 1941, **63**, 2523—2524).—Optimum amounts of HCl and H_2O are described for determination of mixtures of Ca or Ba α- and β-glycerophosphates by $Pb(OAc)_4$–AcOH. R. S. C.

Methyl esters of the higher fatty acids. Separation of small quantities by fractional distillation. F. W. Wyman and C. Barkenbus (*Ind. Eng. Chem.* [*Anal.*], 1940, **12**, 658—661).—Details are given of the construction and operation of a spinning band fractionating column. Me octoate, decoate, laurate, myristate, palmitate, and stearate have been purified by this column, 1—5 g. of material being used. Separation is good, and n_D^{45} vals. are given for the esters. The method can be used for analysis of mixed esters formed from fatty acids from natural oils, even when only 1—2 g. of the acid is available. J. D. R.

Polarographic determination of ascorbic acid. M. M. Kirk (*Ind. Eng. Chem.* [*Anal.*], 1941, **13**, 625—626).—The determination of ascorbic acid at a dropping Hg electrode using a 2% HPO_3 solution as extractant is described. J. D. R.

Errors of Munson and Walker's reducing-sugar tables and the precision of their method. R. F. Jackson and E. J. McDonald (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 767—788, and *J. Res. Nat. Bur. Stand.*, 1941, **27**, 237—255).—Discrepancies between Munson and Walker's (A., 1906, ii, 634) and Hammond's (B., 1940, 889) reducing-sugar tables are attributed to contamination of the Cu_2O with org. matter; Hammond's vals. are confirmed. For the determination of Cu the iodometric method was principally used, NH_4CNS being added near the end of the titration. Schoorl and Regenbogen's modification of the $KMnO_4$ method (A., 1917, ii, 222) gives accurate results. Determination of Cu_2O by dissolution in HCl–aq. $K_2Cr_2O_7$ and titration with $FeSO_4$ (*o*-phenanthroline) approaches in precision the iodometric method very closely at the median and lower concns. of sugar. A. A. E.

Micro-determination of glucose, free and conjugated glucuronic acid. Use of *Saccharomyces sake* No. 6 as fermentative yeast.—See A., 1941, III, 947.

Detection and determination of mono- and di-ethanolamine. I. S. Shupe (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 754—757).—The colour tests described are modifications of Rimini's and Simon's tests for primary aliphatic and *sec.* amines, using Na nitroprusside, $NaHCO_3$, and $COMe_2$ or MeCHO, respectively. Determination is accomplished by prep. and weighing of the *p*-$C_6H_4Br{\cdot}SO_2$ derivatives, extracting that of $NH([CH_2]_2{\cdot}OH)_2$ from an alkaline (NaOH) liquid with $CHCl_3$, and extracting that of $NH_2{\cdot}[CH_2]_2{\cdot}OH$ similarly from the acidified residual liquid. Blank determinations are made with the reagent. The procedure is designed to minimise formation of the disulphonylmonoethanolamine, which is insol. in alkali. An aq. extract of cosmetic creams is first extracted with $CHCl_3$ after addition of acid or alkali (not NH_3). A. A. E.

Micro-determination of betaine and choline. I. Reifer (*New Zealand J. Sci. Tech.*, 1940, **22**, **B**, 111—116; cf. Blood and Cranfield, B., 1937, 174).—A neutral solution (3 c.c.) of choline (**I**) (0·1—5·0 mg.) is treated with 10% KI_3 (5 c.c.) at <10°. After 3 hr. at 0° the ppt. is centrifuged and a suspension of $Al(OH)_3$ (0·5 c.c.) introduced as a top layer. After centrifuging, the supernatant fluid is removed and the reagent washed from the walls of the tube. $Al(OH)_3$ is removed with cold 5% H_2SO_4 (2 c.c.), the fluid removed after centrifuging, and the ppt. dissolved in 90% EtOH (1—3 c.c.). I is determined titrimetrically. Glycine betaine (**II**) (0·3—5·0 mg. in 3 c.c. of 10% NaCl) is treated with H_3PO_4 (0·5 c.c.) and KI_3 (1 c.c.). After 3 hr. at −5° to −10° the ppt. is freed from periodide and H_3PO_4 and titrated as above. In mixtures, only (**I**) is determined by the former procedure whereas both (**I**) and (**II**) are pptd. quantitatively in the latter. Error ±2%. The method is applied to the determination of (**I**) and (**II**) in plants and is limited by the facts that $NHMe_2$, NMe_3, some cyclic bases, and alkaloids are pptd. by KI_3, that the composition of the ppt. depends on the betaine, and that some betaines are pptd. in neutral solution with (**I**). J. L. D.

Determination of leucine and valine by the method of Fromageot and Heitz. E. D. Stacheeva-Kaverzneva (*Biochimia*, 1940, **5**, 513—520; cf. A., 1940, II, 269).—The method is applicable to the determination of valine and leucine, separately, in pure solutions, but not to mixtures of the acids such as occur in protein hydrolysates even after fractionation of the Cu salts. W. McC.

Determination of amino-acids with ninhydrin. A. I. Virtanen, T. Laine, and T. Toivonen (*Z. physiol. Chem.*, 1940, **266**, 193—204; cf. Abderhalden, A., 1938, II, 212).—Free alanine (**I**), valine (**II**), leucine (**III**), *iso*leucine (**IV**), phenylalanine (**V**), and methionine (**VI**) but not the other NH_2-acids of protein or peptides rapidly give theoretical yields of corresponding N-free aldehydes when heated in aq. solution with KH_2PO_4, NaCl, and ninhydrin, $NH_2{\cdot}CHR{\cdot}CO_2H$ yielding $R{\cdot}CHO$. The aldehydes are distilled into aq. $NaHSO_3$ and determined iodometrically. In mixtures of NH_2-acids (protein hydrolysates), (**I**) is separately determined because of the volatility of MeCHO, (**V**) by Kapeller-Adler's method (A., 1933, 1094), and (**VI**) by Baernstein's method (A., 1932, 1149). Application of the procedure to the analysis of zein gives results in agreement with those obtained by other methods, but N contents from (**I**), (**II**), (**III**), and (**IV**) of ovalbumin (7·3 and 15·9% of total N) and cascinogen (5·6 and 14·3% of total N) are > those otherwise determined. W. McC.

Determination of sulphanilamide derivatives.—See A., 1941, III, 1043.

Determination of benzocaine and its separation from acetanilide. E. H. Wells (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 736—739).—Washed $CHCl_3$ extracts of the aq. mixture are shaken with successive portions of 6N-H_2SO_4, combined, and evaporated nearly to dryness; the NHPh·OAc is hydrolysed and titrated by the A.O.A.C. bromide–bromate method. The H_2SO_4 solution and washings are treated with aq. Br in excess, the excess being determined iodometrically and the wt. of *p*-$NH_2{\cdot}C_6H_4{\cdot}CO_2Et$ calc. Recoveries were 98·9—100·3 and 98·2—108·0%, respectively. A. A. E.

Detection and estimation of dihydrorotenone in the hydrogenation products of rotenone. L. D. Goodhue and H. L. Haller (*Ind. Eng. Chem.* [*Anal.*], 1941, **12**, 652—654).—The detection and determination depend on the red colour produced by dihydrorotenone with a reagent of $NaNO_2$–EtOH–KOH followed by H_2SO_4. The colour produced is compared photometrically with a standard of similar and known concn. Rotenone interferes, but the non-toxic by-products of catalytic reduction, rotenonic acid, dihydrorotenonic acid, and dihydrorotenol, do not interfere. J. D. R.

Photo-electric estimation of indole. C. B. Allsopp (*Biochem. J.*, 1941, **35**, 965—966).—The transient colour produced by indole solutions in presence of acidified, alcoholic *p*-$NMe_2{\cdot}C_6H_4{\cdot}CHO$ is measured in a Hilger "Absorptiometer." It is employed for concns. up to 0·002% of indole and the colour is fully developed by heating rapidly just to the b.p. H. G. R.

Colorimetric determination of indolyl-3-acetic acid.—See A., 1941, III, 939.

Determination of piperazine. II. A. Castiglioni (*Z. anal. Chem.*, 1940, **119**, 118—120; cf. A., 1939, II, 398).—Alcoholic solutions of piperazine (**I**) are treated with excess of CS_2–Et_2O (1 : 1), warmed slightly, and kept. (**I**) in $CHCl_3$ is treated with CS_2 alone. The ppt. is washed repeatedly with small quantities of EtOH–Et_2O or $CHCl_3$, according to the solvent used, dried at 105°, and weighed as $C_4H_{10}N_2,CS_2$. The method can be used to determine (**I**) in presence of $(CH_2)_6N_4$, which gives no ppt. with CS_2. Owing to the excessive time required for the complete pptn. of (**I**), Dragendorff's reagent (KI + BiI_3) is unsatisfactory. L. S. T.

Influence of concentration and acid content on crystal form. L. Rosenthaler (*Pharm. Acta Helv.*, 1940, **15**, 257—265).—The influence of concn. of base and HCl on the form of the ppts. obtained by adding (solid) $K_4Fe(CN)_6$ to solutions of 15 bases (synthetic drugs) is described. E. H. S.

Colorimetric determination of pilocarpine and its separation from other alkaloids. I. S. Shupe (*J. Assoc. Off. Agric. Chem.*, 1941, **24**, 757—766).—Pilocarpine (**I**), after hydrolysis of the lactone group with alkali in presence of $NaHSO_3$ to avoid oxidation, is retained in aq. solution and separated from other alkaloids by extraction of the latter with $CHCl_3$, followed by acidification and extraction of (**I**) with $CHCl_3$. It may then be determined volumetrically (1 ml. of 0·02N-acid = 4·16 mg.) or colorimetrically. Helch's reaction involving the formation of (**I**) perchromate, which, unlike $HCrO_5$, is sol. in C_6H_6 and $CHCl_3$, is employed, colour intensity measurements being made, *e.g.*, by means of a Clifford type neutral wedge photometer. The colour is stable for >2 hr. when protected from light. AcOH is most suitable for acidification during development and extraction of the colour. Recoveries were: 97·0—98·6% (volumetric); 97·6—99·0% (colorimetric). A. A. E.